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A STUDY OF THE MECHANISM OF CHEMICAL DISPERSION OF OIL SPILLS

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A STUDY OF THE MECHANISM OF CHEMICAL DISPERSION OF OIL SPILLS

by

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Summary

This report describes a program of research which had the general objective of elucidating the mechanism of chemical dispersion of oil spills, especially under cold marine conditions. The ultimate goal is to put in place a capability of including chemical dispersion as a countermeasure along with other behavior characteristics and countermeasures in oil spill models applicable to temperate and Arctic North American waters. As contributing steps towards this goal three tasks were addressed.

First is a thorough critical review of the chemical dispersion literature with emphasis on seeking a relationship between observed dispersant effectiveness in laboratory tests and in oceanic trials. Whereas high effectiveness is observed in the laboratory, the results of oceanic tests show more variability and frequently performance is very poor, even at high dispersant to oil ratios. This anomaly is discussed.

Second is an experimental laboratory program in which various oils were tested with various dispersants in the MNS, Double Tube, Rotating Flask and Oscillating Hoop systems. Oil properties were measured and analyses were done by gas chromatography, column chromatography and HPLC techniques in an effort to elucidate the role of oil properties and composition as determinants of effectiveness. Some exploratory oil-dispersant mixing tests were done and some synthetic oil mixtures were tested. This work led to the conclusion that in the range of oil viscosities up to a few thousand m.Pa.s or centipoise, the dispersability of an oil is primarily controlled by the ability of the dispersant to access and mix into the oil layer. Waxes appear to retard

mixing and thus reduce effectiveness. At higher viscosities the energy required for viscous deformation of the oil becomes the controlling factor. Aromatics tend to enhance mixing and induce greater effectiveness. A major determinant of effectiveness is the thickness of the oil slick, thin slicks being inefficiently dispersed. A mechanism of dispersion is proposed, an implication of which is that chemical dispersion under cold marine conditions is only marginally more difficult (or requires marginally more dispersant) unless there is a marked increase in oil viscosity as occurs near the pour point.

The third effort was compilation of an oil spill dispersion model consisting of a series of equations easily programmed on a personal micro-computer. This model treats the oil slick as consisting of separate thick and sheen areas and calculates the dispersion effectiveness for any desired dosage and application pattern. The model was calibrated against eleven reported experimental spills and two laboratory test systems (MNS and Rotating Flask) and can give a reasonable representation of the observed performance. The use of the model as a hypothesis against which experimental data can be tested reveals some unresolved anomalies between apparently similar experimental tests. Two major conclusions are (i) that the primary reason for poor oceanic performance is overdosing of sheen and underdosing of thick oil slicks and (ii) that it appears to be possible in principle to link laboratory tests to oceanic conditions by proper separate quantification of turbulent energy regimes which apply first during the dispersion process and later during emulsion resurfacing.

This study is regarded as having contributed towards a better understanding of chemical dispersion of oil spills. The model requires

further validation and probably some structural and parameter-value modification, but it can be used in its present form for preliminary assessments. Some implications of the work are discussed, particularly with regard to further laboratory research and the more effective conduct of experimental spills.

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1. INTRODUCTION.

It is now widely accepted that chemical dispersants have a role in oil spill countermeasures, especially in situations where most damage will result from the presence of a surface slick which may foul birds or important shorelines. Advantages of chemical dispersant application are that it is not necessarily labor-intensive, nor in the case of aerial application does it require the presence of equipment and vessels at the slick site. These advantages become particularly significant in Arctic waters where logistic and human safety constraints are more severe. But there is some doubt about the effectiveness of dispersants under these cold conditions. Indeed, as is discussed later there is doubt about their effectiveness even under temperate conditions.

In recent years considerable effort has been devoted to studying the effectiveness of dispersants in the laboratory and at sea in small trials. A significant conclusion of these studies is that the process is very complex and poorly understood. A basic appreciation of the dominant phenomena controlling effectiveness is still lacking. The result is that comparisons between laboratory tests show puzzling anomalies (presumably because some key unappreciated variable differs between the tests) and comparison of laboratory and oceanic tests show even greater anomalies. Until the basic phenomena are understood it is impossible to compile a mathamatical model based on equations describing these phenomena, although some progress can be made using empirical models.

From an operational viewpoint it is essential to identify the dispersant which is most appropriate for the oil and environmental

conditions which are encountered in a spill situation. Obviously there will be considerable mismanagement if a dispersant is applied which proves to be ineffective. Not only is there a financial penalty and possibly an increase in toxic stress to the ecosystem, but the effort must detract from other countermeasures. There is a compelling incentive to develop a system or systems by which on-scene personnel can obtain reliable information about the likely results of applying chemical dispersants.

It is far from clear at present how this future will unfold but one likely scenario is as follows.

(1) The producer or transporter of a crude oil or petroleum product (the operator) will ascertain the likely behavior and impacts of spills in the relevant region at various times of year. There may be in place a computer model of oil spill behavior incorporating meteorologic and oceanographic information. These models may involve a joint effort of the operator and government agencies such as the Coast Guard or those concerned with environmental protection.

(2) The operator will have tested in advance the effectiveness of various commercially available chemical dispersants on fresh and weathered oils at a range of environmental conditions and will have selected a suitable product for stockpiling. It is possible that some custom formulation of dispersants will be necessary.

(3) In the event of a spill the response team will make measurements and observations of the state of the prevailing oil slick and the environmental conditions, and will then determine the appropriate dispersion procedure. This will presumably take into account the local environmental sensitivities and logistical

constraints.

(4) Dispersion will then proceed from boat or aircraft and the performance will be monitored to determine if further dispersion is warranted. It is hoped that appropriate performance data will be recorded for later analysis to help future decision-making.

Within these four tasks there are certain current inadequacies.

It is not yet clear how the oils should be tested in the laboratory with various products to determine the best dispersant.

It is not known what stockpile volumes are appropriate because of uncertainty about spill volumes and effective dispersant/oil application ratios.

It is not apparent how the response team will determine the likely dispersion effectiveness, but the following forms of information gathering, storage and processing are likely contenders.

- o Tables, graphs, monographs and even slide rules.
- o Data from previous experiences.
- o Computer programs of various levels of complexity ranging from those operable using hand held programmable calculators, to those using portable microcomputers, to those requiring access to remote main-frame computers.
- o Experimental, on-site data obtained by sampling the actual oil and testing it rapidly and simply with the actual dispersant.

Regardless of the method it must incorporate information about the sea surface conditions of turbulence, temperature and possibly ice cover.

The most likely long term solution is judged by the authors to be a combination of these techniques involving human judgement enhanced

by a simple on-site test, an on-site portable computer activity, and linkage to a central computing facility which can provide up to date and predicted weather and ocean current information and ecological advice. If this is accepted, it follows that there is a need to satisfy these three "inadequacies". Underlying all three is the necessity for understanding the basic phenomena. This is best gained by proposing hypotheses, testing them and refining them in the light of experience. From the phenomenological description can flow descriptive equations which can form the basis of a mathematical model, which can then be tested against the experimental data. A successful model can then be deployed in a predictive mode as a countermeasures tool.

The thrust of this report is towards elucidating the phenomena and preparing a tentative mathematical model of the processes involved. Specifically, we compile in Chapter 2 a review of the current literature ending in a statement of the proposed experimental activities. Chapter 3 describes these experimental activities, and the results, with discussion, are given in Chapter 4. Chapter 5 is a synthesis of the findings into a descriptive statement of the phenomena, leading to a tentative mathematical model. Finally, in Chapter 6 certain conclusions are reached and some recommendations made for future work.

In closing, it must be emphasised that obtaining an adequate scientific description of the phenomenon of chemical dispersion of oil slicks is likely to be a long and demanding task. This effort is viewed as one small step in that long journey.

2. LITERATURE REVIEW.

2.1 Literature Sources

The literature on chemical dispersion is unfortunately distributed between a number of types of publications which greatly vary in approach and in accessibility. The list of references provided at the end of this report is regarded as being fairly complete up to March 1985. The principal literature sources are

(1) Texts such as those authored or edited by Malins (1977), Cormack (1983), Wardley-Smith (19), Geyer (1980), Engelhardt (1985), and Jordan and Payne (1980)

(2) The two-yearly proceedings of the "Oil Spill Conference" held in the U.S. and organized and published by the American Petroleum Institute, the U.S. Coast Guard and the U.S. Environmental Protection Agency. The most recent was held in February 1985 in Los Angeles.

(3) Two ASTM reports, the first being STP 659 edited by McCarthy Lindblom and Walter (1978) recording the proceedings of a 1977 Williamsburg symposium, and the second STP 840 edited by Allen (1984) being the proceedings of a 1982 symposium held at West Palm Beach.

(4) The Proceedings of the Arctic Marine Oilspill Program Technical Seminar, held annually in Edmonton and published by Environment Canada. The latest (seventh) was held in June 1984.

(5) Various reports of Government agencies, industry consortia and individual companies and research groups, notably Warren Spring Laboratory in the U.K., PFO and IKU in Norway, Delft Hydraulics Institute in the Netherlands, USEPA, Environment Canada, U.S. Coast Guard, IFP in France, and the U.K. Government.

(6) Reports of the Baffin Island Oil Spill (BIOS) project

sponsored by Environment Canada in cooperation with a number of other agencies.

(7) Papers in the scientific literature, notably Oil and Petrochemical Pollution and Marine Pollution Bulletin.

It should also be noted that work on the phenomenon of natural dispersion (in the absence of applied chemicals) is highly relevant to this study as is work on the interfacial properties of oil-water systems, sea surface turbulence and breaking wave phenomena.

An attempt has been made here to gather and review this literature with particular emphasis on the relationship between laboratory and oceanic effectiveness.

2.2 Laboratory Effectiveness Tests.

At least 22 laboratory chemical dispersant effectiveness tests have been documented (Mackay et al. 1984). These tend to fall into several groups.

Several "tank tests" have been reported in which a volume of 2 to several hundred litres of water is agitated by pumping, spraying or mixing under reproducible conditions. Oil and dispersant are added in a prescribed manner and the amount of oil dispersed is measured. Most relevant here is the MNS test described first by Mackay et al. (1978) at the 1977 ASTM symposium and later by Mackay and Szeto (1981). Other references include Crowley (1984), Byford and Green (1984), Lewis et al(1985), Ness and Norland (1983) and Ness (1984). Another tank test of interest is the "hoop" test in which a hoop is used to generate radial waves on a water surface by vertical oscillation. The advantage of this test is the accessibility of the oil and its natural containment in the centre of the water surface by the inward radial

action of the waves. This test has been described by Mackay et al. (1984), Cox and Schultz (1981) and Lewis et al. (1985).

Several "shake-flask" tests have been proposed, notably the Warren Spring test and the Labofina test, in which 0.25 to 2.0 L of water is agitated in a flask, usually by rotating. Again oil and dispersant are added and dispersion measured. Most well documented is the Warren Spring test, for example by Martinelli (1984), Byford and Green (1984), and Crowley (1984). Mackay and Hossain (1983) have described an "at-sea" shake flask test.

A cascading weir or flume test has been described by Mackay et al. (1984) in which water, oil and dispersant are continuously flowed down an inclined flume and the effectiveness measured at this steady state condition. The steady state nature of the condition facilitates observation and measurement.

Finally, several measurements or observations of interfacial behavior have been reported which provide valuable information about an aspect of the dispersion process. Examples are the SRI test or dropweight test described by Rewick et al. (1980, 1981, 1982, 1984), the Kruss or spinning drop technique described by Mackay and Hossain (1982) and elsewhere. Bobra et al. (1984) have described a "Double Tube" test system in which the aim is to view the dispersion process in detail while making only approximate effectiveness measurements.

An important and surprisingly often neglected aspect of these tests is the measurement of oil droplet size. Byford et al.(1984) and Lewis et al. (1985) have convincingly demonstrated that the ability to generate "small" droplets of slow Stokes' Law rising velocity is a critical determinant of effectiveness. Unfortunately

the measurement of droplet size is experimentally demanding and expensive.

Another aspect for which there is inadequate literature is the effect of the oil's chemical composition on effectiveness. It has long been clear, and for obvious reasons, that the oil's physical properties of viscosity and density are important, although the effect of these variables is not always consistent. Canevari (1934, 1985) has shown that two oils of similar physical properties may display quite different dispersabilities, presumably because of differences in composition. These differences may be due to the hydrocarbons (e.g. alkanes, aromatics, waxes, asphaltenes) or due to natural surfactants, or both. Photolysis of an oil apparently alters the nature or quantity of these surfactants and affects emulsifying behavior (Thingstad and Pengerud 1983).

Finally, some laboratory wind-wave tank tests have been described by Delvigne (1985) in which an attempt was made to simulate the hydrodynamic conditions applying to a previous oceanic test. Bouwmeester (1984) has undertaken similar tests of natural dispersion under carefully defined hydrodynamic conditions.

This literature shows that the following factors influence effectiveness

- oil type (viscosity, density, chemical composition)
- dispersant type
- dispersant to oil ratio
- temperature
- water salinity
- configuration or geometry of the oil-dispersant contacting

system

- o turbulence during dispersion
- o water column turbulence as a factor combining with droplet rising velocity to control the duration of dispersion
- o presence of ice

In addition to these primary variables, the secondary variables of droplet size, rising velocity, coalescence, partitioning of dispersant between oil and water, and time of measurement of effectiveness play additional roles in influencing the effectiveness.

There has been considerable debate and some discontent about the present laboratory test systems. The two which are most frequently used are the MNS and the Rotating Flask. The latter was originally devised by Labofina and has been modified and improved by Warren Spring Laboratory in the U.K. and by IVL in Sweden. These two tests are successful in discriminating consistently between the very ineffective and the effective dispersants, but they do not rank the effective dispersants consistently. There has been considerable debate about this issue (Crowley 1984, Mackay et al. 1984, Ness 1984) and the general conclusion appears to be that the Rotating Flask test is preferred where a quick, inexpensive, reproducible method is sought. The MNS test (which has been adopted as a standard by Environment Canada, 1984) is more complex, suffers from some irreproducibility problems due to wave damping, but is possibly more realistic in that it does have an agitated water-air interface. It thus yields more information, but at the price of more experimental effort, and it demonstrates the existence of complexities, the significance of which are difficult to assess. Probably the debate between the tests is largely irrelevant because neither may adequately simulate oceanic conditions to the desired level of fidelity.

The recent work of Lewis et al. (1985) is particularly enlightening. These workers studied the MNS, Rotating Flask and Hoop systems and also measured interfacial tensions and droplet size spectra, and from this deduced interfacial areas. The turbulence levels in these tests vary considerably but comparison is more meaningful when turbulence is regarded as making two separate contributions namely

(i) generating the dispersion, i.e. forming new surface area as enhanced by the low interfacial tension which induced by the surfactant.

(ii) maintaining the dispersion by eddy turbulence or mixing in the water column.

The first contribution can be assessed by measuring droplet size or area, especially immediately after dispersion. All systems have this type of turbulence. The second contribution can be assessed by measuring the decay of dispersed concentration with time, i.e. the extent of resurfacing. In the Rotating Flask test the conditions are essentially stagnant, but in the other tests (and in the ocean) there is turbulence which can serve to retard resurfacing. An oil may thus be equally dispersed by the MNS and Rotating Flask tests but may resurface in the Rotating Flask test but not in the MNS test resulting in an apparent difference in performance.

Lewis et al. (1985) concluded that the Rotating Flask performance is controlled by the resurfacing process, whereas the MNS performance is controlled by the dispersion process, there being adequate eddy mixing to suspend even relatively large oil drops. The tests are thus measuring quite different phenomena and it is not surprising that the results differ. In this work we use all the available test systems, Rotating Flask, MNS, Double Tube, and Hoop in the hope that each test will contribute some different or unique insight into the nature of the phenomena. Further, we devote some effort to elucidating the effect of oil composition and oil-dispersant mixing on effectiveness, largely because they are neglected areas.

2.3 Oceanic Tests.

A considerable number of oceanic tests has been undertaken and described, but with varying degrees of completeness. In some cases the primary aim was not to measure effectiveness but some related variable such as oil concentration under the slick.

A particularly useful review is that of Nichols and Parker (1985) who have compiled data from some 55 field trials and four actual incidents. Here we review briefly the test spill findings.

The first reported tests were those of Cormack and Nichols (1977) in which dispersant was applied to two 0.5 m^3 slicks from a boat at a dispersant to oil ratio (DOR) of 1/20. At higher wind speeds the dispersant was effective in clearing the oil from the water surface.

The 1978 New Jersey spill has been described by McAuliffe et al. (1980). Four Murban and La Rosa crude oil spills (1.67 m^3) were treated at 14 deg.C and at 5-12 knots by an unidentified dispersant at DORs of 1/10 and 1/5 from a helicopter. The Murban slick was "almost completely" dispersed while the La Rosa dispersion was about 50%.

A sequel test in 1979 in Southern California was described by McAuliffe et al (1981). Eight Prudhoe Bay spills (1.6 and 3.2 m^3) were treated with an unidentified dispersant at 10-15 knots at DORs of 1/20 to 1/70 using a boat and a plane. The effectivenesses as measured by integrating water concentrations were very variable, specifically 5%, 8%, 11%, 62%, 45%, 60% and 78%.

In 1978, Green et al. (1982) of Seakem undertook 3 small spills of 0.2 to 0.4 m^3 at Royal Roads, B.C. in a boom using Corexit 9527 at a DOR of 1/10. There was no significant dispersion.

In 1981 a spill was treated off St. Johns, Newfoundland and described later by Gill (1983). No effectiveness results were

obtained.

In 1982 a series of 7 spills of Statfjord oil were studied by Lichtenthaler and Daling (1983) with reports by Lichtenthaler and Daling (1983) and Ness and Norland (1983). Three dispersants were tested (Corexit 9527, Finasol OSR5 and BP 1100WD) in the field and in the laboratory. Conditions were 7-12°C, 5-13 knots, 2 m^3 spills dispersed at DORs of 1/10 and 1/15. The effectivenesses were 6%, 17%, 19%, 22% and 2%, with two untreated controls.

Also in 1982 a joint U.K. Government-Esso spill was undertaken in the North Sea and described in a report by Cormack (1982). The Arabian Light crude oil (20 tonnes) was treated in calm waters at 7 knots at 10-11 deg.C with Corexit 9527 at an average DOR of 1/10, but in fact with a variation from 1/2 to 1/45. The dispersant "did not lead to significant and permanent removal".

Delvigne (1984, 1985) of the Delft Hydraulics Laboratory undertook a test of Statfjord and light fuel oil with Finasol OSR5 at 2-8 m/s wind speed and 18 deg.C. One spill of premixed Statfjord oil at a DOR of 1/10 to 1/30 was 100% effective. The other spill dispersed at only approximately 2% per hour. Corresponding wind wave tank tests at similar hydrodynamic conditions were more effective. Tests were conducted to determine if this difference was due to evaporation, mousse formation or photolysis but these processes could not account for the magnitude of the difference.

Bocard, Gatellier and Croquette (1981) have reviewed the series of Protecmar spills in French waters. The oil volumes were 2 to 4 m^3 and were treated with a variety of dispersants, usually under fairly calm conditions. It was concluded that although some of the oil

dispersed, little diffused beyond 1 m depth.

Bocard et al. (1983) reviewed the Protecmor 3 tests with 6.5 m^3 of light fuel oil. Dispolene 32S dispersant applied at a DOR of greater than 1/3 caused 50 percent dispersion within 4 hours with only scattered sheen remaining. Another dispersant caused considerable spreading of the oil but less dispersion.

A spill off Halifax was organized in 1983 by a Canadian Government -Industry group (COAATF) and some preliminary results presented in a number of papers at the 7th AMOP Conference in 1984 and by Gill et al (1985). Spills of 2.5 m^3 of Alberta sweet blend crude oil were treated with Corexit 9550, Corexit 9527 and BP MA700. The results can be summarized as follows

Corexit	9527	DOR	1/27	Wave height	0.4m	Effectiveness	1-4%
"	9550	"	1/8	"	0.3m	"	15-21%
BP MA	700	"	1/9	"	1.2m	"	9-41%

It was concluded that the measurement of effectiveness by water column sampling is suspect and that effectiveness is influenced by sea state.

The BIOS spills as reviewed for example by Blackall and Sergy (1983) convincingly demonstrated (as was subsequently demonstrated by others) that by premixing oil and dispersant it is possible to accomplish very effective dispersion. More details of the experimental technique used in that study have been reported by Mackay et al. (1983).

In 1984 a series of small 4 litre experimental spills was conducted in the Beaufort Sea by MacWatt et al. (1985). A local crude oil was spilled between parallel booms which were allowed to lie along

the wind direction. An attempt was made to collect the undispersed oil in order to obtain an unequivocal determination of effectiveness. The results were, for a variety of reasons, not quantitatively conclusive, but dispersion did occur when the oil and dispersant were premixed.

In 1984 a series of spills was performed in Norwegian waters, the results being given by Lichtenthaler and Dahling (1985).

Four 10 m^3 slicks were dispersed with Corexit 9527 added after 1, 2 and 4 hours and in one case with premixing. Control slicks were also studied. The DOR values calculated for the thick slick varied from 1/50 to 1/80 with 1/33 for the premixed case.

In the first case (W1) it was estimated that 90% of the oil (2 mm thick) was present in 14% of the total area of 3.2 ha. The theoretical DOR was 1/22 but the thick slick DOR was only 1/75. No effectiveness estimate could be made but oil concentrations of 10 to 60 ppm were obtained indicating significant dispersion.

In the two other aerially dispersed slicks (W2 and F2) the thick slick was about 1 mm thick and the areas considerably larger (15 ha and 35 ha). Significant dispersion occurred as indicated by the concentrations of up to 40 ppm.

The premixed (P2) slick dispersed well giving concentrations of up to 182 ppm

It was concluded that in addition to the dispersion effect, some surfactant remains with the oil to act as a water in oil emulsion breaker, and that dispersants enhance spreading rates. Evaporative loss has little influence on dispersion at least over a few hours weathering.

It was apparent that when the dispersant was applied accurately to the relatively thick oil patches dispersion ensued, confirmation being obtained both visually and by concentration measurement. A noteworthy point was that the parts of the treated slick which did not disperse immediately spread to about three times the control slick area and could not be detected the next day. It appears that "natural" dispersion was enhanced by the treatment or perhaps there was delayed dispersion.

In 1982 100 tonnes of oil was spilled at Halten Bank, Norway (Audunson et al. 1984, Lange 1985). Comprehensive measurements were made of the slick behaviour including natural but not chemical dispersion.

Some large outdoor wind-wave tank studies by Goodman (1984) and McNeil et al. (1985) showed that with Norman Wells crude oil and Corexit 9527 and 14 cm waves 30-40% dispersion resulted. With larger 28 cm waves 100% dispersion was reached. Ice appeared to enhance dispersion.

Although there is a lack of well-documented evidence that dispersants has been successful when applied to actual spills there are indications that their use has proved successful. Cormack (1983) reports a number of incidents in which the use of dispersants was beneficial. Linton and Koons (1983) reported that dispersants had a significant effect on the Ixtoc slick. Herding of the oil took place over short distances, i.e.less than 1 m but not over the entire swath width of 73 m. A significant amount of dispersion took place.

Nichols and Parker (1985) reviewed the Olympic Alliance, Elevi V, Betelgeuse and Sivard tanker incidents in which from 35 to 900 tonnes

of dispersant were used. The effectiveness was difficult to judge but in at least some cases the use was regarded as beneficial.

From a consideration of these results certain general conclusions can be drawn.

When a given oil-dispersant system at a specified DOR is tested under controlled conditions at sea and in the laboratory there is usually a much higher efficiency in the laboratory. There have been occasions in which sea tests have been successful, but in many cases the effectiveness is poor. There are several possible explanations.

(1) The oil weathers, photolyses or forms emulsion. This seems unlikely in view of Delvigne's results. Numerous laboratory tests indicate that these effects are relatively slight and can not alone account for the magnitude of the difference.

(2) The oceanic turbulence is not simulated in the laboratory. Oxygen transfer coefficients at sea and in the laboratory are comparable, thus to the extent that this measure of turbulence is appropriate, conditions are not dissimilar. The tank studies of Delvigne and Goodman appear to approximate oceanic conditions, and showed good performance. The successful tests reported by McAuliffe, Lichtenthaler and Dahling suggest that this is not the major cause of the discrepancy.

(3) There are systematic measurement errors in one or both systems. This seems unlikely because the presence of oil on the surface is obvious. It is most unlikely that all laboratory systems are in error.

(4) The mechanism of oil-dispersant contacting is important and is different in the two cases. This appears to be the most likely

explanation, if only by elimination of the others. If this is correct, then in many cases the oceanic application mechanism is such that the oil and dispersant contact, mix or interact inefficiently, i.e. much dispersant is wasted. Support for this comes from the observation that when application conditions are well controlled, as in large tanks or in the 1984 Norwegian tests, dispersants perform well. Premixing results in high efficiency both in the laboratory and at sea, thus further implicating the contacting phenomemon as the basic problem.

An important point may be that the time-scale of oceanic dispersion is longer i.e. dispersion may be delayed. Evidence for this comes from the fairly successful record of applications to actual spills and the Protecmor and 1984 Norwegian observations of delayed disappearance. Perhaps it is too demanding to expect dispersion immediately and a major role of the dispersant is to facilitate natural dispersion, by for example thinning the slick. The turbulence damping of a large thick oil slick may appreciably inhibit natural dispersion.

One definite conclusion from these spills is that the measurement of effectiveness at sea is very difficult and some effort should be devoted to improving measurement techniques. Ultimately it is desirable to measure both the oil which is dispersed and the oil which remains on the surface and establish a mass balance. Measurement of oil concentrations beneath slicks are subject to large errors which arise from heterogeneities in time and space and insufficient sampling.

Another factor affecting oceanic tests may be that by necessity the slick volumes and areas are relatively small and "hard to hit"

from the air. For example the thick slick of 1984 WI Norwegian test was only 320 x 15 m (0.48 ha). In the Halifax trial the thick slick area was about 10,000 m^2 (1 ha). Delvigne's slick had a total area of 6 ha but it is likely that much of the oil was concentrated in 0.5 to 1.0 ha. In general the thick areas are elongated and about 0.5 to 1.0 ha which is a fairly small target for an aircraft. It is presumably much easier to apply dispersant accurately to the thick slicks in a larger real incident.

The primary implication of these findings for this study is that it is important to elucidate the nature of the oil-dispersant contacting process and its role in altering effectiveness. For this reason considerable effort was devoted to testing the following hypotheses.

A first hypothesis follows from the observation that under laboratory conditions the dispersant is deliberately and carefully applied to the oil surface and usually to a thick oil slick. In the Rotating Flask test the oil layer is 1.5 mm thick while in the MNS test it is 2.6 mm thick. A typical thickness in a hoop test is .1 mm. At sea, however, the slick thicknesses are often 0.1 to 1.0 mm and much of the area consists of sheen which is less than 0.01 mm thick. The dispersant is usually applied randomly over the entire slick and much may land on sheen.

Aerially applied dispersant drop diameters are generally in the range 0.1 to 0.5 mm and often 0.35 to 0.50 mm (Lindblom and Cashion 1983). The drops may fall 20 m in a matter of seconds thus their velocity is such that they have a considerable impact on collision with the slick. Many may penetrate the slick. This could cause

ineffective oil-dispersant mixing. The largest drops will arrive at the slick first, may rupture the oil slick and induce herding. Later drops may land on the dispersant-water surface from which oil has been herded. In many cases the application of a swath of dispersant produces a striking effect on slick appearance, but this may be due in part to herding. It should be noted that this herding is over distances of centimetres, not tens of metres or the swath width. The herding phenomena has been frequently observed and has been described by Canevari (1984) who also observed that the less viscous dispersants tend to "roll off" viscous oils. In the laboratory systems the dispersant which rolls off or penetrates the slick is still in fairly close proximity to the oil and some may return or migrate back to the oil water interface. At sea where the water/oil volume ratio is much larger this return is less likely. In laboratory systems some effectiveness is achieved even when the dispersant is added to the water rather than the oil. Accordingly in this study we explore this oil-dispersant mixing process and the herding phenomena.

A second hypothesis is that the dispersant drops are often unable to contact the volume of oil which they can potentially disperse. Bobra et al. (1984) concluded that Corexit 9527, when applied optimally, was able to disperse 45 times its volume of crude oil. For illustrative purposes we can consider a dispersant drop of diameter D applied to a slick of thickness T at a DOR of 1/N, N being typically 16 plus or minus a factor of two . For convenience we use micrometres (um) as the base unit of length, area and volume and assume for simplicity that the drops are cubes. Further, we assume that 1 volume of dispersant is capable of dispersing X volumes of oil, a value for X being adopted for illustrative purposes.

Now a cubic drop of volume D3 has the potential to disperse XD^3 volumes of oil which will have an area of XD^3/T. If we regard that area as a square it will be of side $\sqrt{XD^3/T}$, thus for optimal application the drops should land this distance apart. In practice, because the application ratio is 1/N, and X usually exceeds N (i.e. more dispersant is applied than is necessary) the drops will fall closer at a distance of $\sqrt{ND^3/T}$. We can now consider the magnitude of this distance in relation to the size of the dispersant drop. We postulate that there is a "zone of accessible oil" around the fallen drop which is some multiple of the drop size. For example, it appears reasonable that a drop could spread over an oil area perhaps 6 times its diameter. We designate this multiple (here suggested as 6) as M.

Now the actual ratio M which is achieved is the drop-to-drop distance divided by D. For optimal application it is thus $\sqrt{XD/T}$ and for actual application it is closer and $\sqrt{ND/T}$. We can now explore the magnitude of these M values by considering combinations of D and T

using an illustrative value of 16 for N. The ratio M then becomes $\sqrt{16D/T}$ or $4\sqrt{D/T}$. If T equals D then M is 4, which seems to be a reasonably attainable spread area. If D is less than T then M is less than 4 and high efficiency may be expected (i) because the dispersant drops fall in larger numbers and closer together and (ii) because they are less likely to cause slick penetration and herding. If D exceeds T there is a possibility of much of the oil receiving no dispersant because it is too distant from a drop. Further herding is likely, with subsequent dispersant landing on water.

What emerges is the rather obvious conclusion that ideally the dispersant drops should be comparable in size to the slick thickness or smaller. If they are much larger each drop, if it is to be effective, must exert a "zone of influence" which is a considerable multiple of its diameter. There is a constraint caused by aerial droplet drift considerations which requires that the droplets exceed 100 μm, but this in turn implies that slicks of thickness less than 100 μm may be treated ineffectively.

But in practice much of an oil slick area is occupied by thin oil slicks or sheen. If for example there are thick and thin slicks which differ in thickness by a factor of 10 and the thin slick is 10 times the area of the thick slick then there will be equal volumes in both thick and thin slicks. The thin oil will receive approximately 90% of the dispersant. Now if the average DOR is 1/16, i.e. N is 16, then the thin slick value of N will be 16 x 0.5/0.9 or 9 (a high DOR value) but the thick oil will have an N of 16 x 0.5/0.1 or 80. The result is that the thick slick is severely underdosed and the thin slick is overdosed. But the thin slick M value will be higher because of its

thinness, thus that dispersant which is applied to it may be less effective. The overall conclusion is that variations in slick thickness inherently result in ineffective application. This may have occurred in the sea trials, indeed it was acknowledged to have occurred in the U.K.-Esso and other trials. It is significant that in the successful Norwegian 1984 trial care was taken to apply most of the dispersant to the thick oil at the leading edge of the slick. This problem does not, of course, occur when the oil and dispersant are premixed.

One conclusion from this hypothesis is that in any experimental spill it is essential to measure the slick thicknesses, areas and dispersant dosages for thin and sheen areas separately. Measuring the average thickness and dosage and the total area yields little useful information.

It is thus hypothesised that there are several phenomena which can combine in sea tests to reduce effectiveness:- herding, inadequate mixing of oil and dispersant, failure of the dispersant drops to have a sufficient accessible quantity of oil and over-dosing of thin slicks with corresponding underdosing of thick slicks.

3. EXPERIMENTAL SECTION.

3.1 MNS System.

Figure 3.1 is a schematic diagram of the MNS Apparatus, a full description of which has been reported by Mackay and Szeto (1980, 1981).

In this study, a new orifice plate (ID of 20 mm) was used to measure the pressure drop. The correlation between the "old" (ID = 25.4 mm) and "new" design is given in Figure 3.2. This new orifice plate conforms better to standard orifice plate designs.

Six litres of synthetic seawater were poured into the clean vessel which was in a temperature controlled bath. After the seawater reached the desired temperature, the lid was fitted and the containment ring was lowered until it was half-way immersed in water. The air flow was then turned on and regulated to produce a pressure drop across the orifice plate which corresponded to the desired turbulence level. After a steady wave motion had developed, 10 mL of oil was added to the water surface inside the containment ring. Dispersant was then delivered dropwise on to the oil surface from a digital pipette. A minute and a half after applying the dispersant on to the oil surface, the containment ring was lifted. After 10 minutes of agitation, a 500 mL sample was taken and analysed for oil content by visible spectrophotometry using the oil being tested for calibration.

The percentage of oil dispersed was then calculated and recorded. In some cases the presence of oil or dispersant at the air-water interface interferes with momentum transfer from air to water and wave damping occurs. This reduces the turbulence level and gives anomalously low dispersion percentages. When this occurred it was noted

and the results interpreted accordingly.

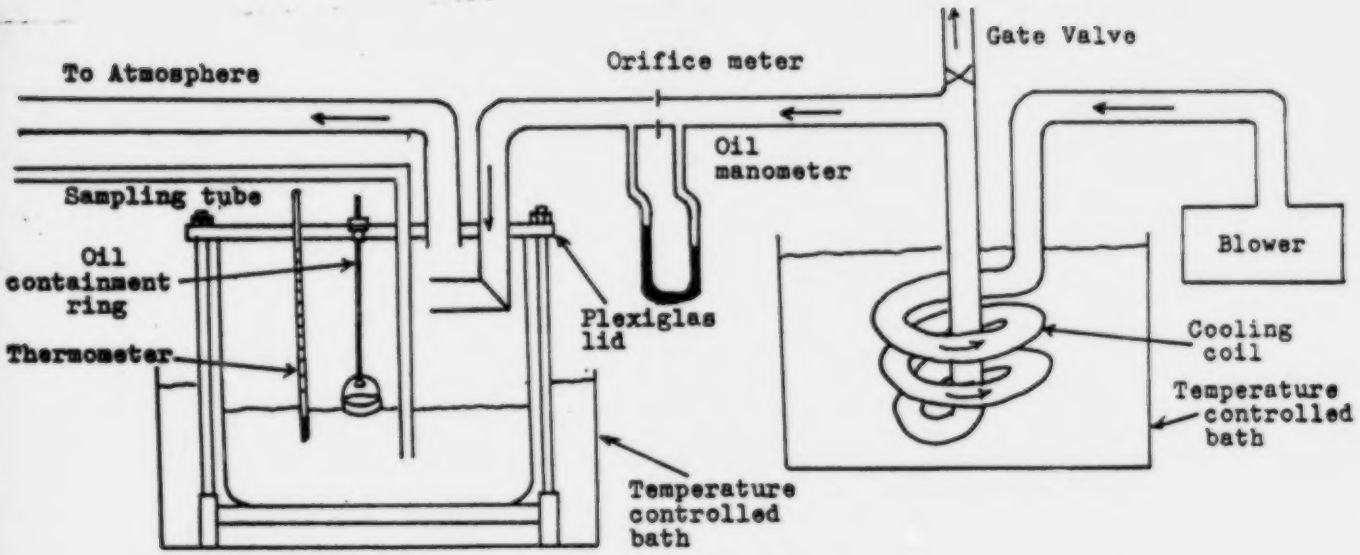


Figure 3.1: Schematic Diagram of MNS Apparatus

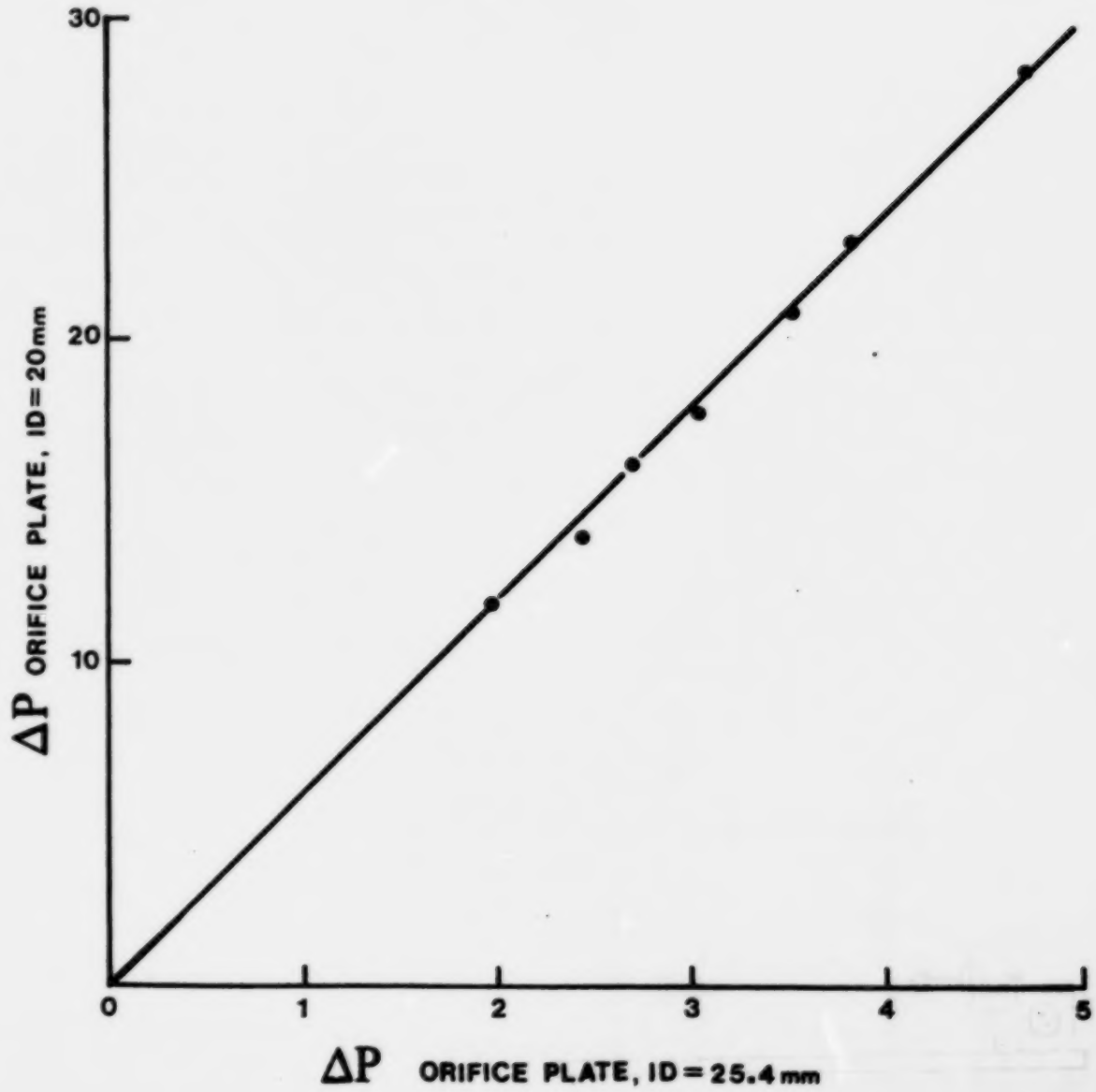


Figure 3.2: Calibration Curve For Orifice Plate

3.2 Rotating Flask System.

The rotating flask apparatus used in this study is essentially the Warren Spring laboratory test (Crowley 1984) and consists of a motor driven rack into which the 250 mL separatory funnel can be positioned and rotated at 34 RPM about a horizontal axis. A schematic diagram of this equipment is shown in Fig. 3.3.

A 250 mL capacity separatory funnel (Kimax, U.S.A.) was filled with 250 mL seawater at 15 deg. C. The separatory funnel was placed in a rotatable rack, 5 mL of test oil (slick thickness of 1.46 mm) was added through the pipette on to the water surface and was allowed to rest for one minute. A known amount of dispersant was then placed as evenly as possible over the surface of the oil.

After applying the dispersant, the separatory funnel was immediately stoppered and secured in position. When the time on the stopwatch showed 2.5 minutes from the addition of the oil, the rotation was started at 34 rev/min for exactly 2 minutes. After one minute standing in a vertical position to allow some resurfacting a 50 mL sample was taken and analysed for oil content by visible spectrophotometry. The percentage dispersed was then calculated and recorded.

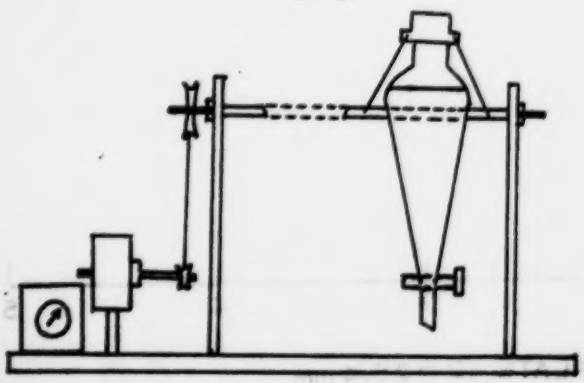


Figure 3.3: Rotating Flask System

3.3 Double Tube or Bobra System.

This system has been described fully by Bobra et. al. (1984) but a brief description is given here. The apparatus shown in Fig. 3.4 contains a water surface which is subject to a radially inward flow. Oil is placed on this surface and is contained near the centre out of contact with the walls. There is shear under the oil surface to facilitate dispersion. The upper and lower interfaces can be viewed and photographed. Measurements of effectiveness of dispersion can be obtained by recovering the remaining oil from the water surface.

The apparatus consists of a 5.4 cm inner diameter by 19 cm high glass tube fitted into a 9.2 cm inner diameter by 29 cm high glass tube. Six radial glass supports on the inner tube ensure that it remains centred within the larger tube and stable during flow. Both tubes are tapered at the lower end: the inner tube being connected to a 7 mm inner diameter tube and the outer tube to a 2.5 cm inner diameter opening. This opening is sealed with a rubber stopper with one hole to accommodate the 7 mm tube of the inner tube and the other to accommodate another 7 mm inner diameter glass tube which is sealed at the end and is perforated with small holes to allow the flow of water into the apparatus to be evenly distributed. This results in a uniform flow of water up between the two tubes, then down inside the inner tube.

The apparatus was connected to a constant level tank with Tygon tubing by adjusting the needle valves which controlled the volumetric flowrates in and out of the apparatus. The water level in the apparatus can be regulated. By trial and error, the water level was set to 1 cm above the top of the inner tube. At this level, the shear

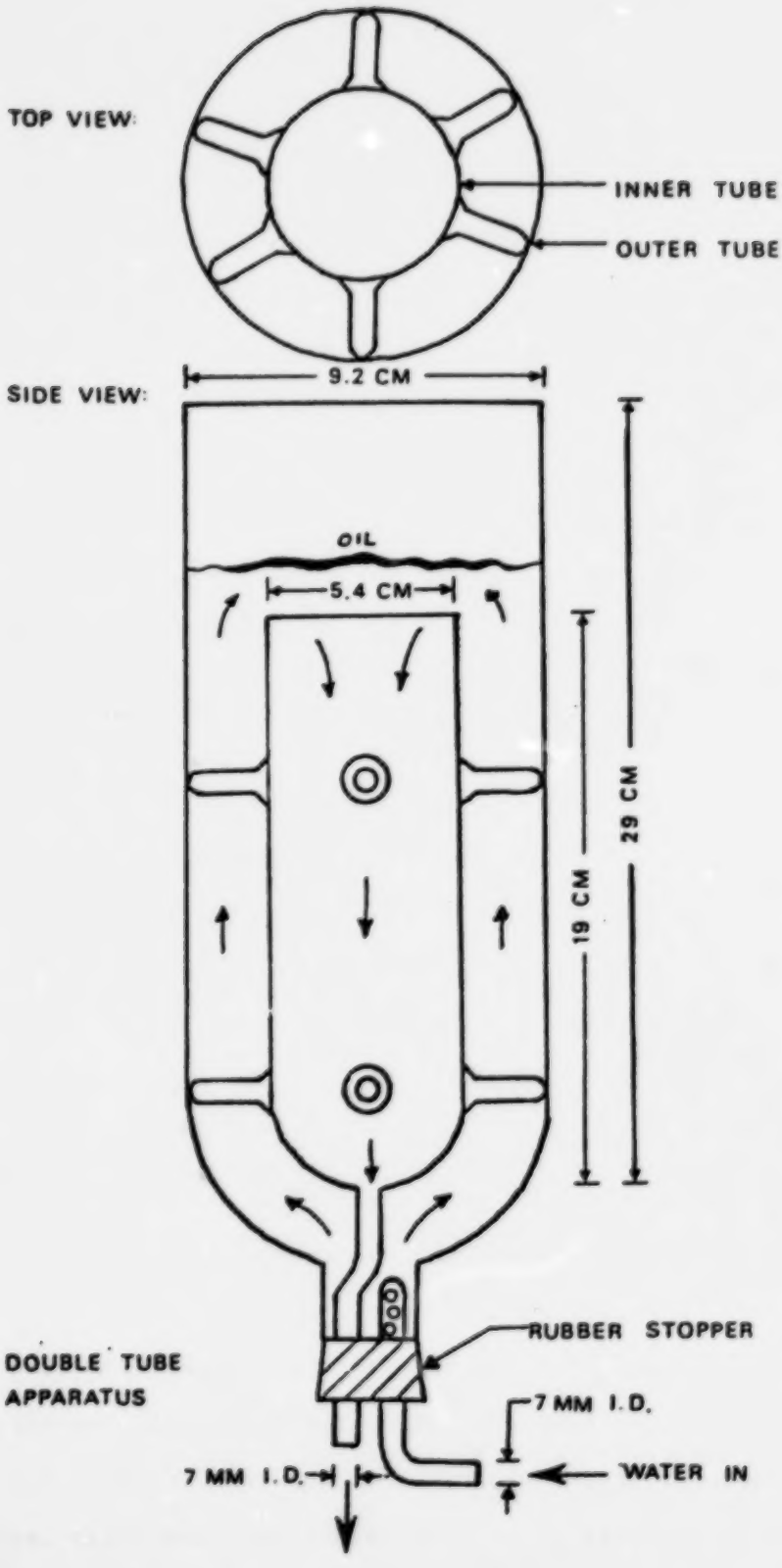


Figure 3.4: Double Table System

created by the water flow was just less than that necessary to shear droplets from the oil slick, thus no natural dispersion occurred before the application of dispersant to the oil. All experimental runs were performed at these conditions.

A steady flow of water (water salinity 33 ppt and 20 deg. C) at 3.5 L/min was started through the apparatus. A known volume of oil was added to the water surface, and allowed to spread over the water surface for 2 minutes. The dispersant was then added as drops to the oil surface from a digital pipette with the tip located at a height of 2.5 cm above the slick.

Various dosages of dispersant were applied in a single application of a series of drops, each of volume approximately 0.01 cm3 and diameter 2.6 mm, to slicks of 3 different volumes, 1.2 cm3 (0.18 mm thick); 2.4 cm3 (0.36 mm thick); and 4.8 cm3 (0.72 mm thick). These thicknesses are nominal, and are based on a diameter of 9.2 cm. In practice the diameter was slightly smaller and the thickness greater by a few percent. The amount of oil remaining in the slick was measured 10 minutes after adding the dispersant.

To measure the amount of oil dispersed, the water contained in the inner tube was slowly drained off until less than 10 mL of oil and water was contained in the tube. This mixture was then drained directly into a 10 mL graduated volumetric cylinder, separated into layers, and the amount of oil recovered was determined. The apparatus was then dismantled and rinsed with 40 mL of methylene chloride. The methylene chloride layer was separated from the water layer, filtered and analysed for oil content in a spectrophotometer at a wavelength of 540 mm using an appropriate calibration curve.

To explore the effect of added mixing energy some tests were done in which the water was stirred by a 7 mm diameter rod bent into a "crooked" shape such that its end swept out a circle of 3.4 cm outside diameter and it penetrated 0.5 cm into the water. The stirring speed was 200 RPM. The stirrer was turned on 30 seconds after the dispersant was applied and agitation continued for 45 seconds.

The oils used were Norman Wells Crude Oil and a blend of 70% No. 6 fuel oil 30% No. 2 fuel oil. The dispersants used were Corexit 9527, Corexit 9550 and BP MA700.

3.4 The Hoop Apparatus.

The hoop apparatus shown in Figure 3.5 consists of a 37 cm diameter by 30 cm deep open plastic tank containing a 20 cm depth (0.024 m^3) of 30 g/L salt water at 15 deg. C. An oscillating ring of diameter 31 cm acted as a wave generator. It was made from 0.6 cm diameter tubing bent into the form of a hoop. This hoop was just immersed in the water and could be raised and lowered at a rate of 200 vertical strokes per minute driven by a 12 volt Chrysler windshield wiper motor powered by a 12 volt car battery. A sampling tube was immersed at a depth of 8 cm below the water surface.

The required volume of oil was poured on to the surface of water. After the oil had risen to the water surface, the hoop oscillation was started. Dispersant was delivered on to the oil surface by a hand operated garden spray. The amount of the dispersant delivered was determined by weighing the spray assembly with an analytical balance before and after spraying. Samples were collected periodically until a constant concentration was reached, usually by 60 minutes. A sample was allowed to drain into a beaker for 15 seconds. Then about 50 cm^3 of sample was collected in a sampling bottle. The contents of the beaker were analysed by spectrophotometry and the percent dispersion calculated and recorded.

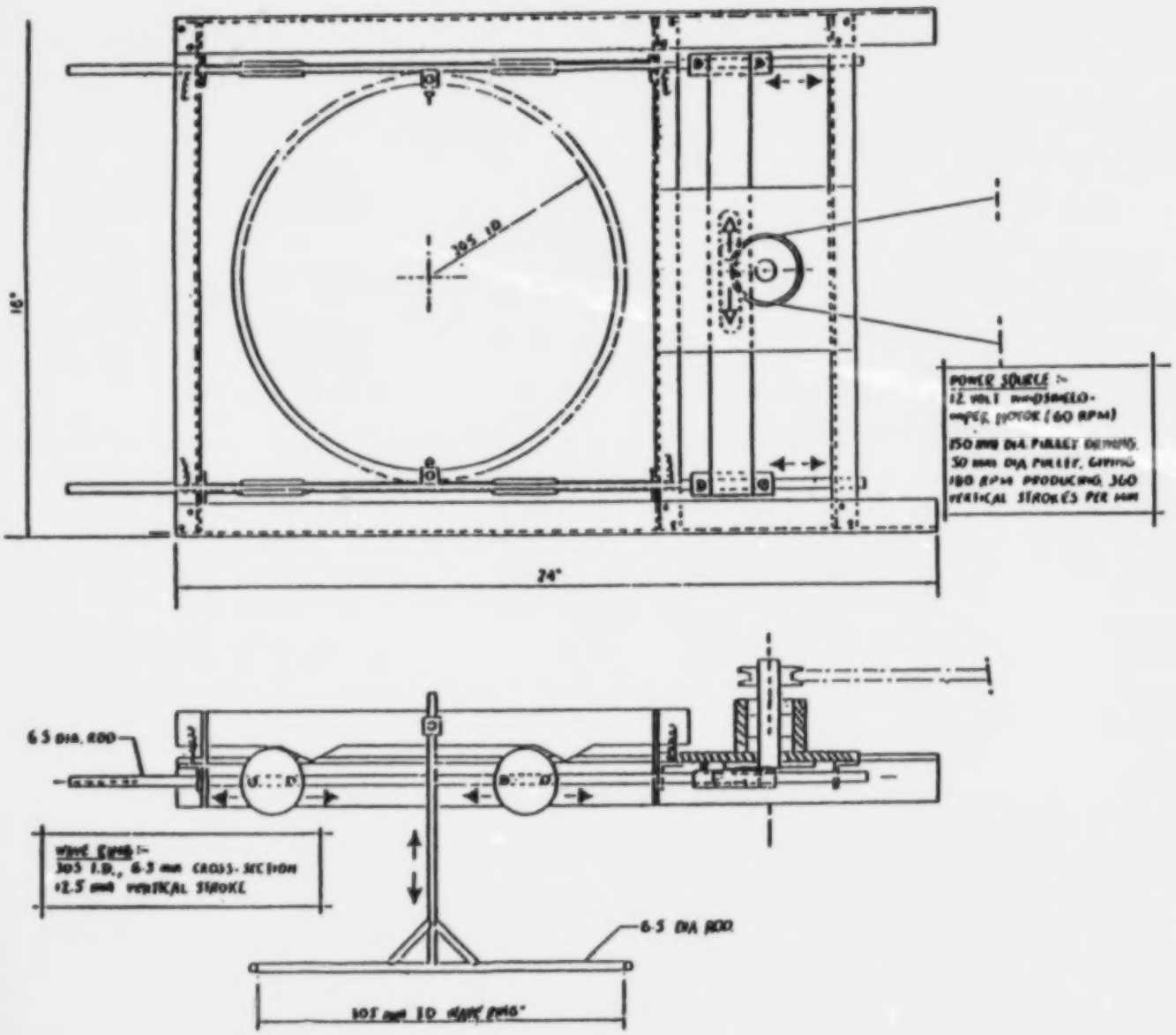


Figure 3.5: Hoop Apparatus

3.5 Analyses of Crude Oils.

G.C. Analyses

GC analyses were done on a Hewlett-Packard 5700A Chromatograph with a 40 m by 0.5 mm id glass capillary SE30 column. Conditions were:- injection port 250 deg.C, detector 300 deg.C, temperature programming at 50 deg.C for 8 min. then 5 deg.C per min to 220 deg.C then hold for 20 min. The flow rate was 1.2 mL/min and the split ratio 1/20. A 3390A integrator was used. The oil analyses are given in Appendix 2.

Column chromatography.

The method of Westlake and Cook (1974) was followed. A preliminary column (1 x 15 cm) was prepared using a slurry of Hyflo Super Cell in pentane. The oil (approximately 0.5 g) was placed on the column and eluted with 50 mL pentane, then 50 mL benzene. The pentane eluate was analysed by a dual column procedure.

3.6 Test Oils.

Crude oil is a complex mixture of hydrocarbons which are classified into several general types including paraffins or alkanes, naphthenes or cycloalkanes and aromatics. In addition the crude oil may contain paraffin-waxes and asphaltenes as well as polar and metal-organic species. It is believed that the composition of the total mixture, in terms of elementary composition, does not vary a great deal, but small differences in composition can greatly affect the physical properties and hence the dispersability of oil when spilled on water.

A number of crude oils were used in this study as listed in Table 3.1. These oils were tested individually, in some cases as mixtures with the pure chemicals and in some cases in a weathered or evaporated condition.

In this study, heptane, cyclohexane, toluene, wax and Cold Lake crude oil were chosen to represent classes of hydrocarbons as mentioned above. By adding different amounts of individual chemical into a particular oil, oil samples of different percent composition can be prepared.

The test oils were prepared by adding a known mass of chemical to a known amount of the oil. This was repeated at different mass proportions and using different chemicals. The oil used were No. 6 fuel oil and Alberta Sweet Blend. The chemicals used were heptane, cyclohexane, toluene, wax and Cold Lake crude oil which has a high asphaltene content (approximately 30%).

Table 3.1 - **Specific Gravity and Viscosity of Test Oils at 15°C**

Oil	Specific Gravity	Viscosity (mPas)
Arabian Heavy	0.8990	94.9
Beaufort Sea	0.8720	7.7
EPS	0.8590	15.2
Fuel Oil #6	0.9645	7733
Kuwait	0.8750	31.0
Lago Medio	0.9270	3600
La Rosa	0.9140	147
Mokoko Albana	0.9420	630.8
Murbau	0.8270	3.3
Norman Well	0.8420	3.6
Prudhoe Bay	0.8930	43.0
Sweet Blend	0.8550	10.9
Base Oil (#2, #6 fuel oil		
Mixture 50 = 50	0.9500	827
7.3 wt. % Toluene	0.9460	293
12.5 wt. % Toluene	0.9410	131
14.4 wt. % Toluene	0.9390	80
17.9 wt. % Toluene	0.9340	59
6.3 wt. % Cyclohexane	0.9360	341
10.2 wt. % Cyclohexane	0.9290	216
17.9 wt. % Cyclohexane	0.9120	93
25.0 wt. % Cyclohexane	0.9020	53

Table 3.1: Continued

Oil	Specific Gravity	Viscosity (mPas)
7.4 wt. % Heptane	0.9260	209
11.8 wt. % Heptane	0.9120	104
14.1 wt. % Heptane	0.9050	80
17.0 wt. % Heptane	0.9085	77
3.2 wt. % Cold Lake	0.9520	845
5.3 wt. % Cold Lake	0.9530	1013
12.7 wt. % Cold Lake	0.9550	1177
22.1 wt. % Cold Lake	0.9610	1307
2.5 wt. % Wax	0.9500	949
5.0 wt. % Wax	0.9480	1653
7.2 wt. % Wax	0.9460	7.2

Table 3.1: Continued

Oil	Specific Gravity	Viscosity (mPas)
Base Oil		
(Alberta Sweet Mix)	0.8360	7.8
1.3 wt. % Heptane	0.8360	6.9
4.0 wt. % Heptane	0.8300	5.4
6.7 wt. % Heptane	0.8270	5.1
7.3 wt. % Heptane	0.8250	4.7
13.0 wt. % Heptane	0.8150	3.7
1.0 wt. % Toluene	0.8360	-
2.0 wt. % Toluene	0.8370	6.8
3.4 wt. % Toluene	0.8385	6.6
8.0 wt. % Toluene	0.8410	5.1
14.0 wt. % Toluene	0.8415	3.9
22.0 wt. % Toluene	0.8440	2.9
1.0 wt. % Cold Lake	0.8380	-
3.1 wt. % Cold Lake	0.8420	-
5.3 wt. % Cold Lake	0.8440	8.0
8.0 wt. % Cold Lake	0.8490	10.2
11.5 wt. % Cold Lake	0.8540	11.6
21.6 wt. % Cold Lake	0.8650	18.6

Table 3.1: Continued

Oil	Specific Gravity	Viscosity (mPas)
2.8 wt. % Wax	0.8370	14.8
5.7 wt. % Wax	0.8930	18.0
8.1 wt. % Wax	0.9200	950
12.3 wt. % Wax	0.9760	5130
2.0 wt. % Cyclohexane	0.8360	-
4.0 wt. % Cyclohexane	0.8355	-
6.0 wt. % Cyclohexane	0.8350	-
8.0 wt. % Cyclohexane	0.8330	-
10.0 wt. % Cyclohexane	0.8320	-
15.5 wt. % Cyclohexane	0.8280	-

3.7 Test Dispersants.

The dispersants used are listed in Table 3.2.

3.8 Water.

In most cases the water was made up as a synthetic sea water containing 33 g/L of sodium chloride in Toronto tap water. In some cases lower salinities were used as detailed later.

Table 3.2: **Specific Gravity and Viscosity of Dispersants at 15°C ± 1°C**

Dispersant	Specific Gravity	Viscosity (cp)
Corexit 9527	1.006	43
Corexit 9550	0.9350	72
BP MA700	0.9780	62.7

4. RESULTS

4.1 Chemical Composition Tests.

The base Alberta sweet mix blend crude oil was blended with various amounts of toluene, cyclohexane, heptane, Cold Lake crude oil (which has a high asphaltene content) and waxes and tested in the MNS and Rotating Flask (RF) systems. The conditions chosen were 15 deg.C and a DOR of 0.004 of Corexit 9527 in order to give a relatively low effectiveness of 23% in the MNS and 13% in the RF systems. The effect of changes in oil chemical composition could then be explored. It should be noted that changes in physical properties also occur, especially with high wax contents.

The RF results are given in Figure 4.1 and the MNS results in Figure 4.2. Toluene has a density higher than but similar to that of the crude oil (0.87 versus 0.84) thus this variable changed only slightly. The toluene viscosity was lower, thus at 14% toluene the viscosity had halved from 7.7 to 3.9 mPa.s. The addition of a small amount of toluene (2 to 4%) apparently increased the RF and MNS effectiveness by only a factor of 1.3 at the most. The MNS results were quite variable. It appears that high toluene contents i.e. viscosities of approximately 3 mPa.s yield low effectiveness.

Heptane causes a reduction in both density and viscosity and has little effect on performance in the MNS system, but a reduction in effectiveness in the RF system, probably because of enhanced resurfacing due to the low density.

Cyclohexane is denser than heptane (0.78 versus 0.68) and apparently enhanced effectiveness in the MNS system by up to a factor of 1.4.

Figure 4.1: Effect of Chemical Additives on Dispersability of Sweet Blend Crude Oil Using the RF System.

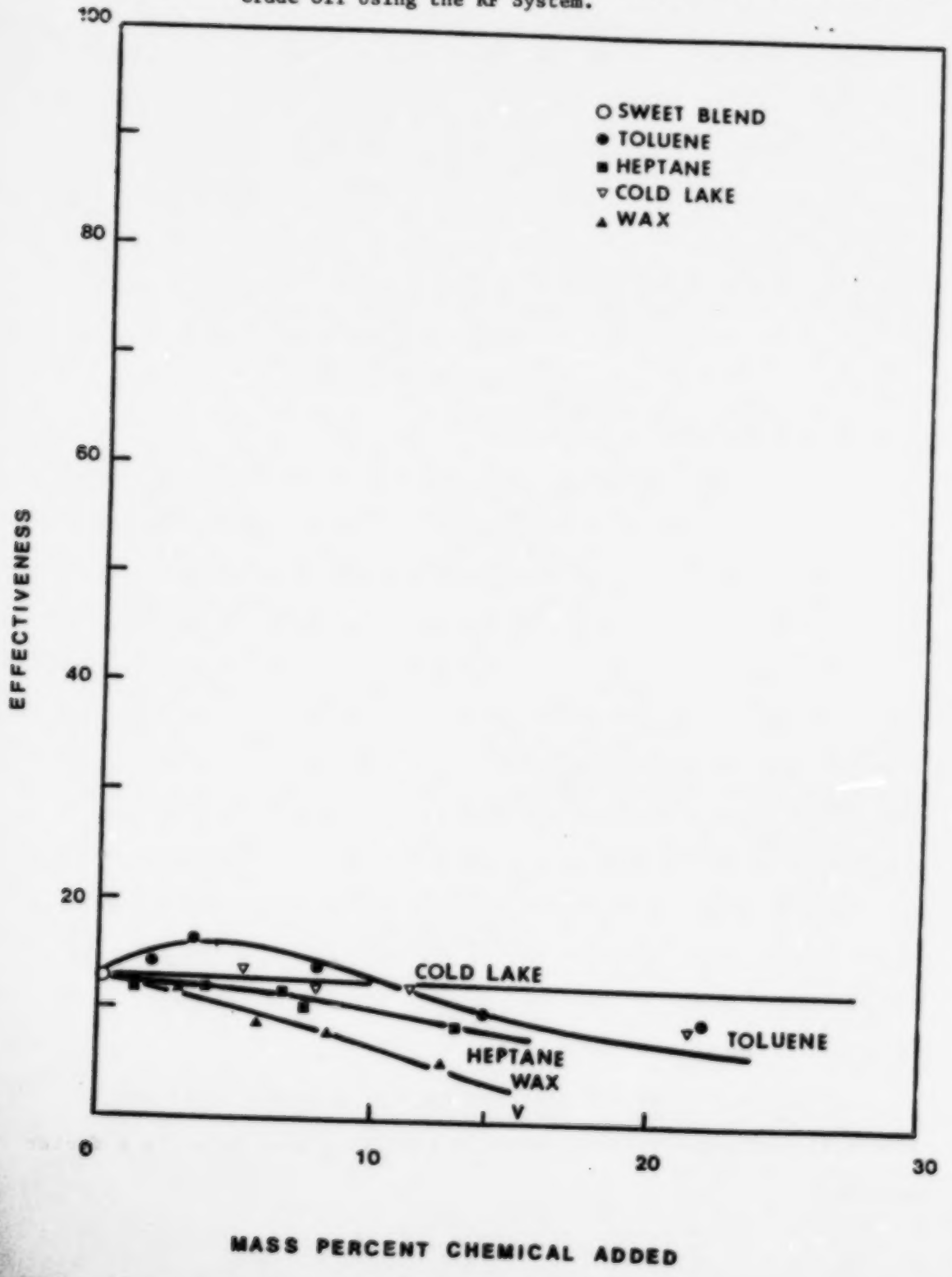
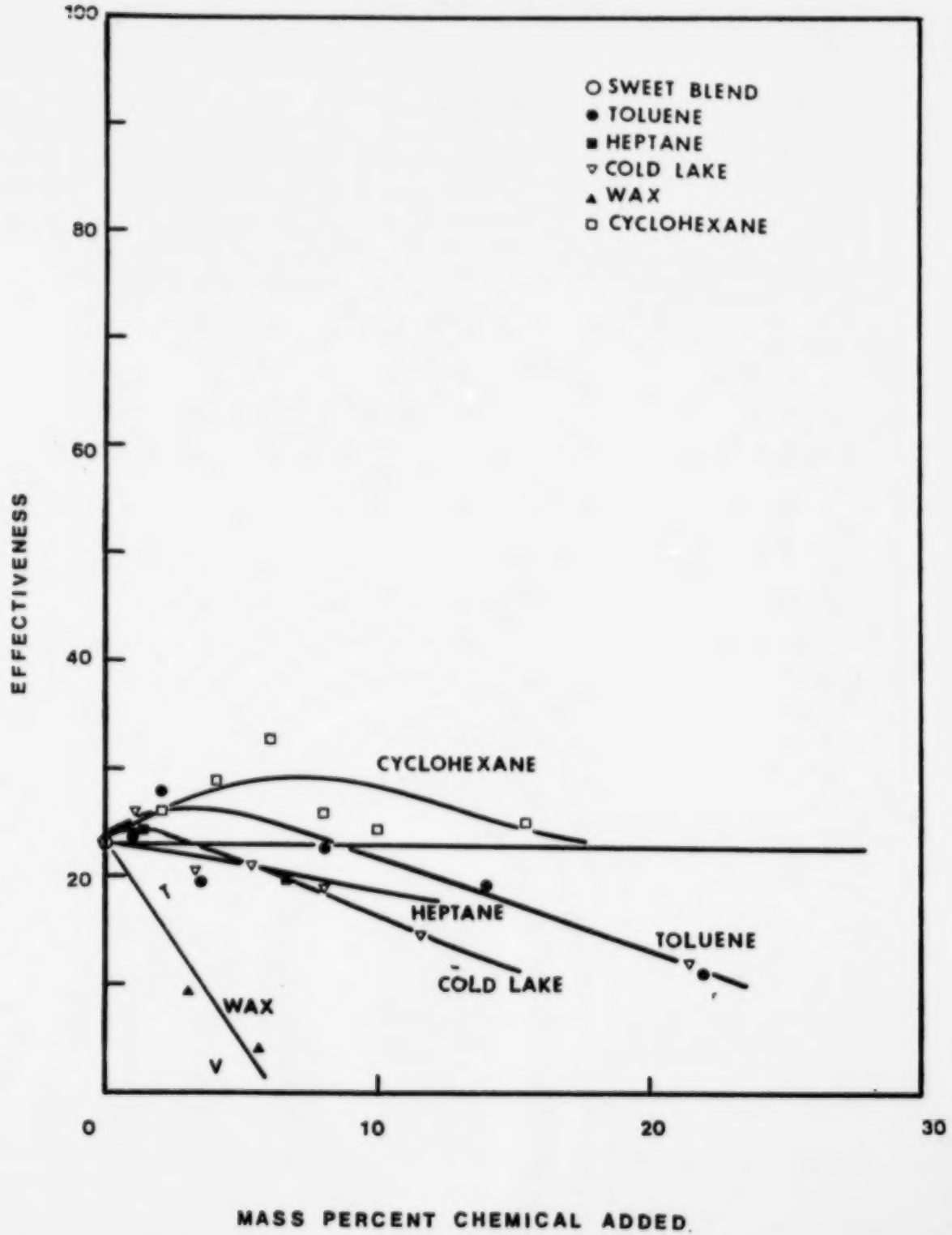


Figure 4.2: Effect of Chemical Additives on the Dispersability of Sweet Blend Crude Oil Using the MNS System.



Asphaltenes as introduced by Cold Lake oil resulted in an increase in density and viscosity but no marked change in effectiveness except at high concentrations (21%) where effectiveness was reduced by a factor of 2. At this condition viscosity had doubled.

Waxes caused a marked increase in both density and viscosity, a 8% mixture having a density of 0.92 and a viscosity of 950 mPa.s. The effect was a marked decrease in MNS effectiveness and a less marked but significant decrease in RF effectiveness. Wave damping occurred with the MNS system suggesting that poor oil-dispersant mixing had taken place. It was noteworthy that even with 12% waxes and a viscosity of 5100 mPa.s the RF effectiveness had fallen only by a factor of 2.4 thus it seems unlikely that viscosity variations in the range 10 to 500 mPa.s will have a profound effect on performance. It seems that in the RF test the energy required to shear the oil and overcome viscous forces may be abundantly available and viscosity only plays a role when it exceeds approximately 1000 mPa.s. It perhaps becomes dominant at 3000 mPa.s. At low viscosities herding may occur and poor mixing is likely to result because of facile penetration of the oil slick by the dispersant.

These results suggest that the conditions selected were such that chemical effects were not particularly significant, all changes being accountable for by density and viscosity. Presumably high density results in a lower Stokes' Law rising velocity and thus higher effectiveness.

A second series of tests was then designed to explore if changing the base oil resulted in a greater sensitivity to chemical

composition. It is possible that the effect of chemical composition is more significant when the oil is more viscous and there is thus a tendency for poorer mixing. Since the mixing is related to the properties of both phases (oil and dispersant) and is a function of their relative densities and viscosities as well as chemical natures or "miscibility" it may be that in low oil viscosity systems it is the more viscous dispersant phase which provides the resistance to penetration by the oil. At higher oil viscosities it may be the oil which offers a resistance to dispersant penetration.

The base oil used was a blend of No. 2 and No. 6 fuel oils (volume ratio 30/70) of density 0.95 and viscosity 827 mPa.s.

These test results are given in Figure 4.3 for the RF test and in Figure 4.4 for the MNS test. As was expected, the effect of additives is more pronounced. The addition of toluene increases effectiveness in both cases suggesting that aromatics enhance the oil-dispersant contacting process. Cyclohexane has little effect but heptane causes a loss of effectiveness in the MNS test. Asphaltenes are interesting because they had opposite effects in the two systems, a reduction in the MNS, but an increase in the RF. This is believed to be due to a reduction of oil-dispersant mixing in both tests, but in the RF test this is counteracted by the reduced resurfacing attributable to the higher density. Waxes cause a reduction in both systems, especially in the MNS test. The RF reduction would probably have been larger but for the increase in density which retards resurfacing.

It would have been interesting to test the role of surfactants but no "model compounds" were available. Canevari (1985) has suggested that natural surfactants interact with the chemical

Figure 4.3: Effect of Chemical Additives on the Dispersability of Fuel Oil Mixture Using the RF System.

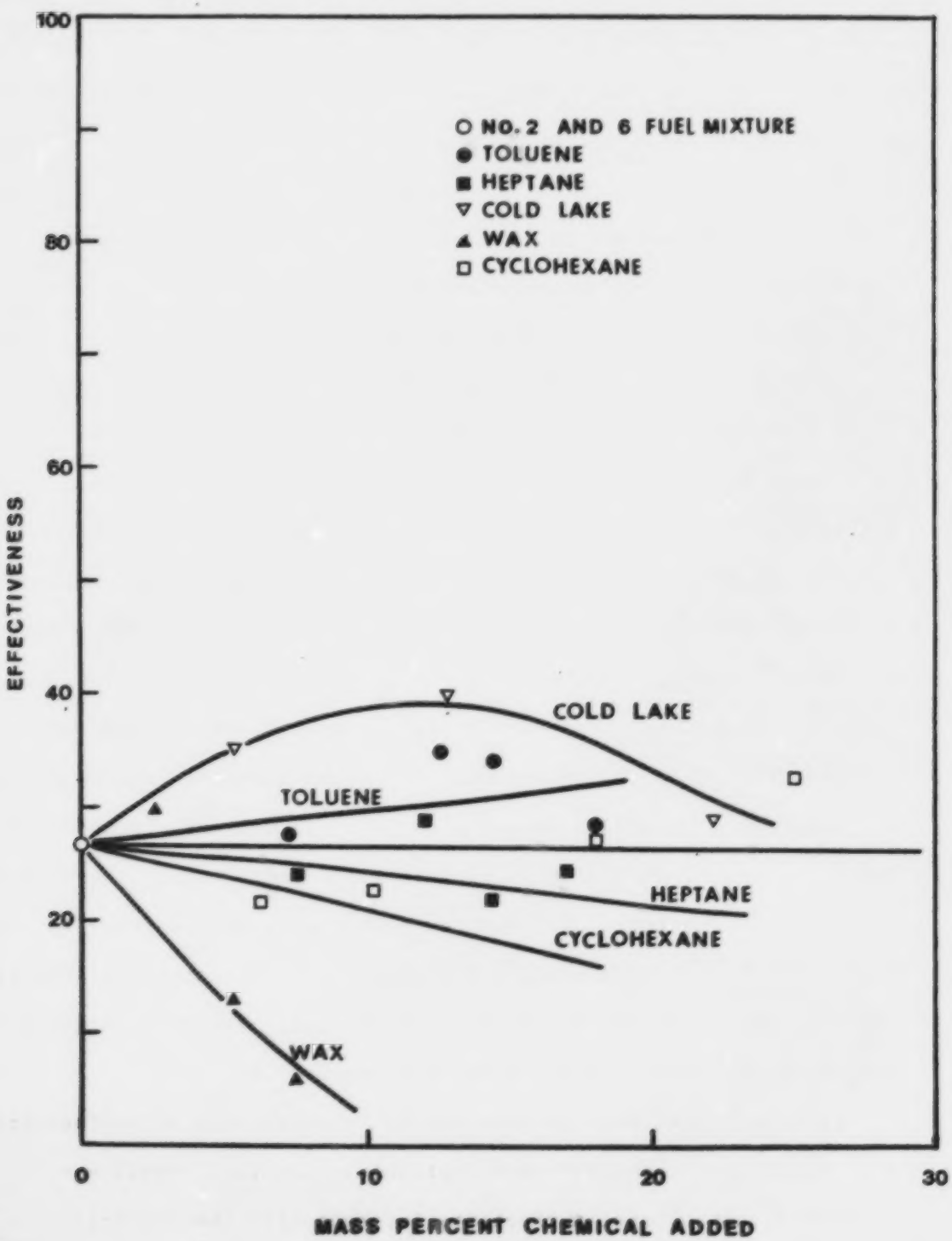
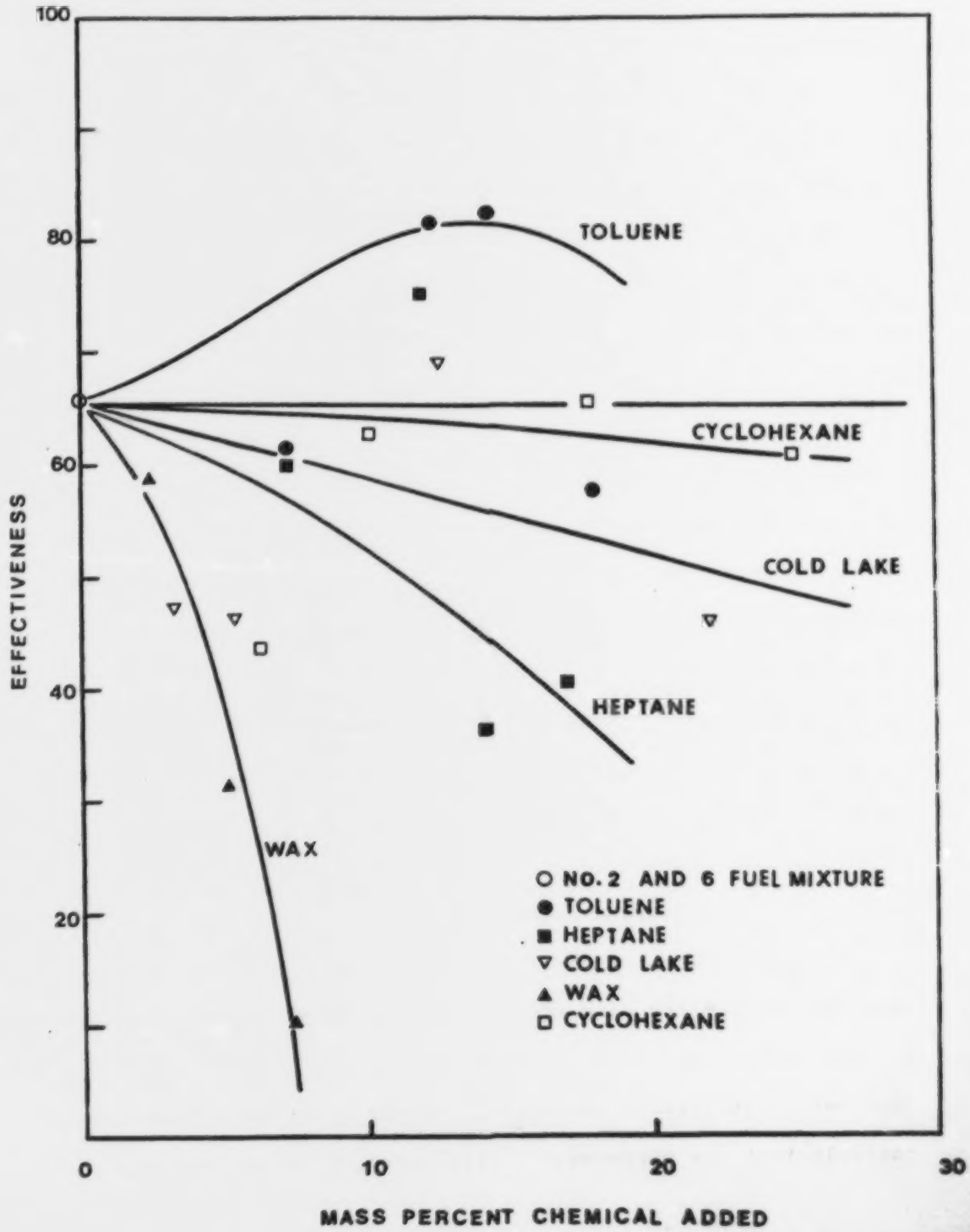


Figure 4.4: Effect of Chemical Additives on the Dispersability of Fuel Using the MNS System.



dispersants to affect overall performance. It is striking however that even very small quantities of chemical dispersants (e.g. DCR of 1/500) have a significant effect on dispersion, thus the amount or efficiency of the natural surfactants must be quite low. It is possible that the primary role of these surfactants is not to reduce interfacial tension but is to facilitate wax accumulation at the oil-water interface thus retarding the dispersant-oil mixing process.

As a further exploration of the effects of chemical composition, ten oils were subjected to HPLC analyses to obtain a breakdown into fractions of aromatics, polars, saturates and asphaltenes. The results are given in Table 4.1 along with viscosity, density and percent dispersed by the MNS and RF tests. Ideally a multivariate analysis should be conducted but this is confounded by the undoubted relationships between for example viscosity, density and asphaltene contents. Plots were prepared to seek interactions but no clear dependencies emerged. Unfortunately there were no wax analyses. It is possible that this is the most important single variable.

The general conclusions from this study are

(1) As has been documented by Lewis et al. (1985) the RF test is very sensitive to resurfacing velocity and thus tends to give good performance for dense oils. The MNS test is less sensitive to density because of the continued turbulence.

(2) The effect of chemical composition of the oil appears to be more significant for more viscous oils in which mixing is more difficult and the time of oil-dispersant contacting is longer. Light oils are less sensitive because the mixing process is more rapid and it is possible that the dispersant "falls through" the oil rapidly.

Table 4.1: Properties Composition and Dispersability of Selected Crude Oils at 15°C and DOR of 0.0150.

Oil	S.G.	Viscosity CP	Percent Oil Dispersed Corexit 9527 MNS	Corexit 9527 RF	Corexit 9550 MNS	Corexit 9550 RF	HA700 MNS	HA700 RF	Composition Mass% Arom	Polar	Sat.	Asph.
FPS	0.8590	15.2	30.1 36.0	28.8 28.0	24.4 41.0	8.9 —	28.5* 50.8	18.4 19.0	7	1	89	4
La Rosa	0.914	147	28.6	20.1 19.6	53.3	20.4 22.5	53.2	37.2 36.4	20	3	68	9
Arabian Heavy	0.8990	94.9	29.6 29.4	24.7 26.0	65.4	25.0 23.3	35.2	30.8 32.6	18	2	71	9
Mokoko Albana	0.9420	630.8	40	28.4 31.7	32.1	11.2 9.7	23.9	19.2 19.5	16	4	78	2
Kuwait	0.8750	31.0	37.2 31.5	25.2 24.3	92.4 79.7	33.4	53.0 49.9	35.6	18	2	75	5
Sweet Blend	0.8550	10.9	40.3	30.9 25.2	55.7 50.5	8.1 9.4	52.5	26.0 24.9	11	1	86	2
Norman Wells	0.8420	3.6	64.8	29.6 24.5	58.7	10.2 8.1	61.3	9.1 8.1	8	2	89	1
Prudhoe Bay	0.8930	43.0	45.9	25.3 22.0	71.7	15.6 14.5	43.1	28.4 28.0	—	-	—	-
#6 Fuel	0.9645	7733	2.2* 1.3*	3.3	27.2	19.9	10.9	11.3	—	-	—	-
Murban	0.8270	3.3	92 74.5	62.6 68.7	135 113	26.0 20.9	141 142	28.9 28.2	—	-	—	-
Bios Crude (Lago Medio)	0.9270	3600	10.5	—	16.1	—	7.0	—	—	-	—	-
Beauford (Sea Tarsuit)	0.8720	7.7	95.1 84.5	43 49.4	35.0 40.8	21.9 21.9	54.4 61.0	13.3	3	1	95	1

* Test conducted at 15°C and D/O ratio of 0.0150

(3) Waxes appear to be the primary inhibitor of oil dispersant mixing.

(4) Aromatics appear to enhance mixing.

(5) The effect of viscosity is relatively slight in the range studied.

(6) No simple chemical characterization of a crude oil is likely to be successful as a predictor of effectiveness, thus it will probably be necessary to test each oil with the dispersants which are proposed to treat it.

4.2 Double Tube (Bobra) Tests.

Some of the results given below have been presented at the 1984 AMOP Technical Seminar, however, further tests were done to obtain more data.

When Corexit 9527 was tested with 2.4 mL of Norman Wells crude oil approximately 50% of the oil was dispersed at a DOR of 0.01, i.e. each volume of dispersant dispersed 50 volumes of oil (Figure 4.5). If V is the volume of oil dispersed and v is the volume of dispersant applied then V is approximately 50v. This line is shown in Figure 4.5. If the fraction of oil dispersed is F and the initial oil volume is Vo then

$$F = V/Vo = 50v/Vo = 50D$$

where D is the dispersant to oil ratio (DOR). This line reaches 100% when D is 1/50. But in fact there is a fall off in effectiveness as F reaches 70% and the slick thins below 0.01 cm from its initial 0.036 cm. One method of expressing this fall-off mathematically is to use an exponential function as suggested by Mackay et. al. (1984) of the form

$$F = 1 - \exp(-50D)$$

When 50D is small the exponential can be expanded into a series and gives the simple linear equation

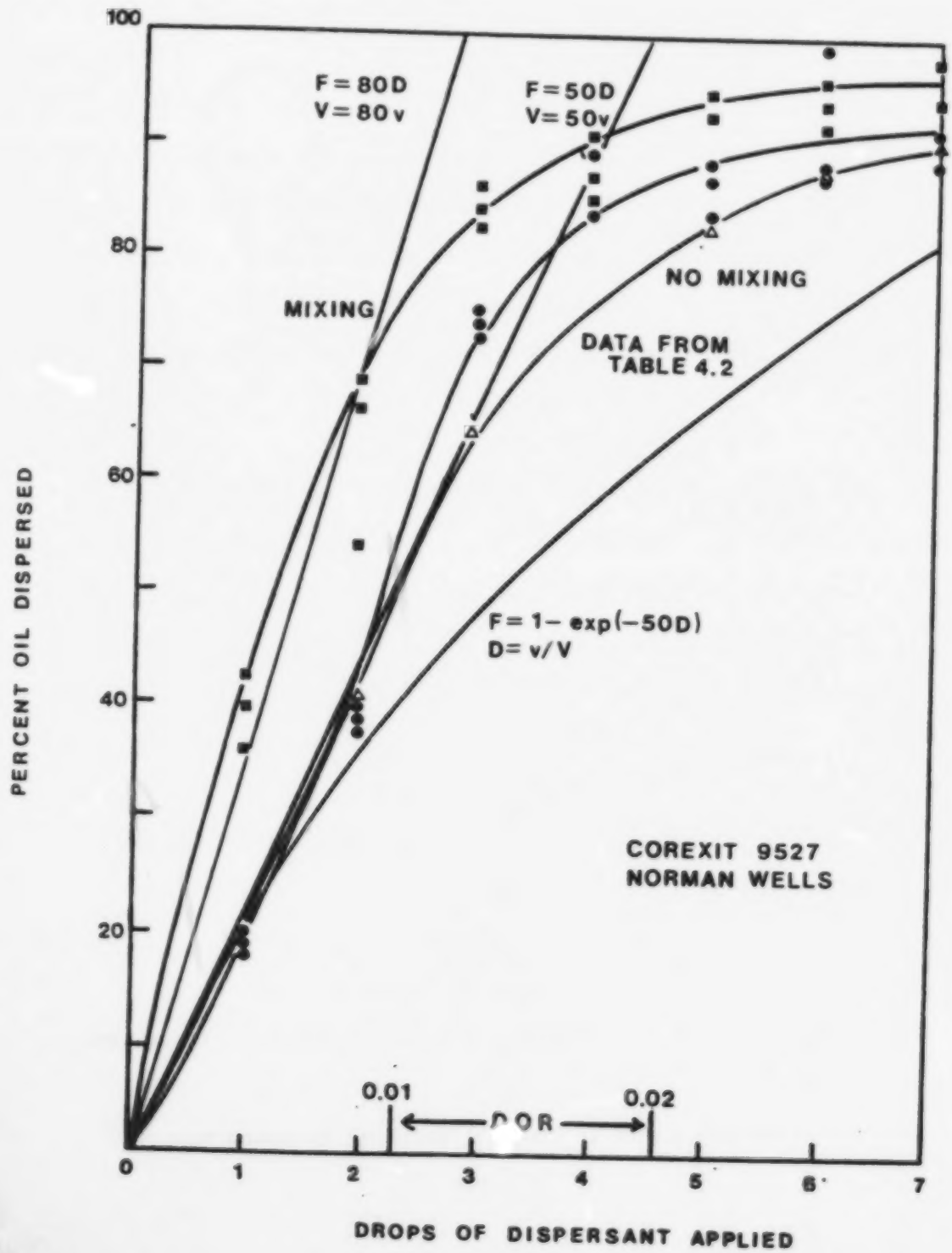
$$F = 50D + \text{higher terms}$$

This exponential line is shown in Figure 4.5 and is fairly satisfactory up to 40% but it badly underestimates the effectiveness at higher values.

When mixing energy is introduced the line steepens to

$$F = 80D$$

Figure 4.5 Double Tube System Dispersion of 2.4 mL Norman Wells Crude Oil Using Corexit 9527



and the dispersant is now more effective.

Figure 4.6 shows corresponding data for an initially thinner slick of 0.018 cm (1.2mL). The "50D" line is shown and satisfactorily describes the data up to 50% dispersion or again 0.01 cm. Similar results were obtained with a 4.8 mL oil slick. For Corexit 9527 and the more viscous 70/30 fuel oil mixture the performance was better with mixing, but poor in the absence of mixing (Figure 4.7). Apparently the higher oil viscosity introduces a "mixing resistance".

Corexit 9550 was ineffective on Norman Wells crude oil without mixing, but was very effective on the 70/30 fuel oil (Figures 4.8 and 4.9). It is a hydrocarbon based dispersant designed to perform well on dense, viscous oils.

BP MA 700 was very effective on Norman Wells crude oil up to 80% dispersion but it had little subsequent effect (Figure 4.10). It also performed well on the 70/30 fuel oil, especially when mixed (Figure 4.11).

Examination of these results suggests that it is very desirable to "match" oil to dispersant. This is best illustrated by the relative performances of Corexit 9527 and 9550 on Norman Wells crude oil and the 70/30 fuel oil in which the following percentages were dispersed for 3 drops with no mixing

	Norman Wells	fuel oil
Corexit 9527	75	30
Corexit 9550	20	95

Clearly there is an incompatibility between Corexit 9527 and 70/30 fuel oil and between Corexit 9550 and the light Norman Wells crude oil.

Figure 4.6: Double Tube System Dispersion of 1.2 mL Norman Wells Crude Oil Using Conexit 9527

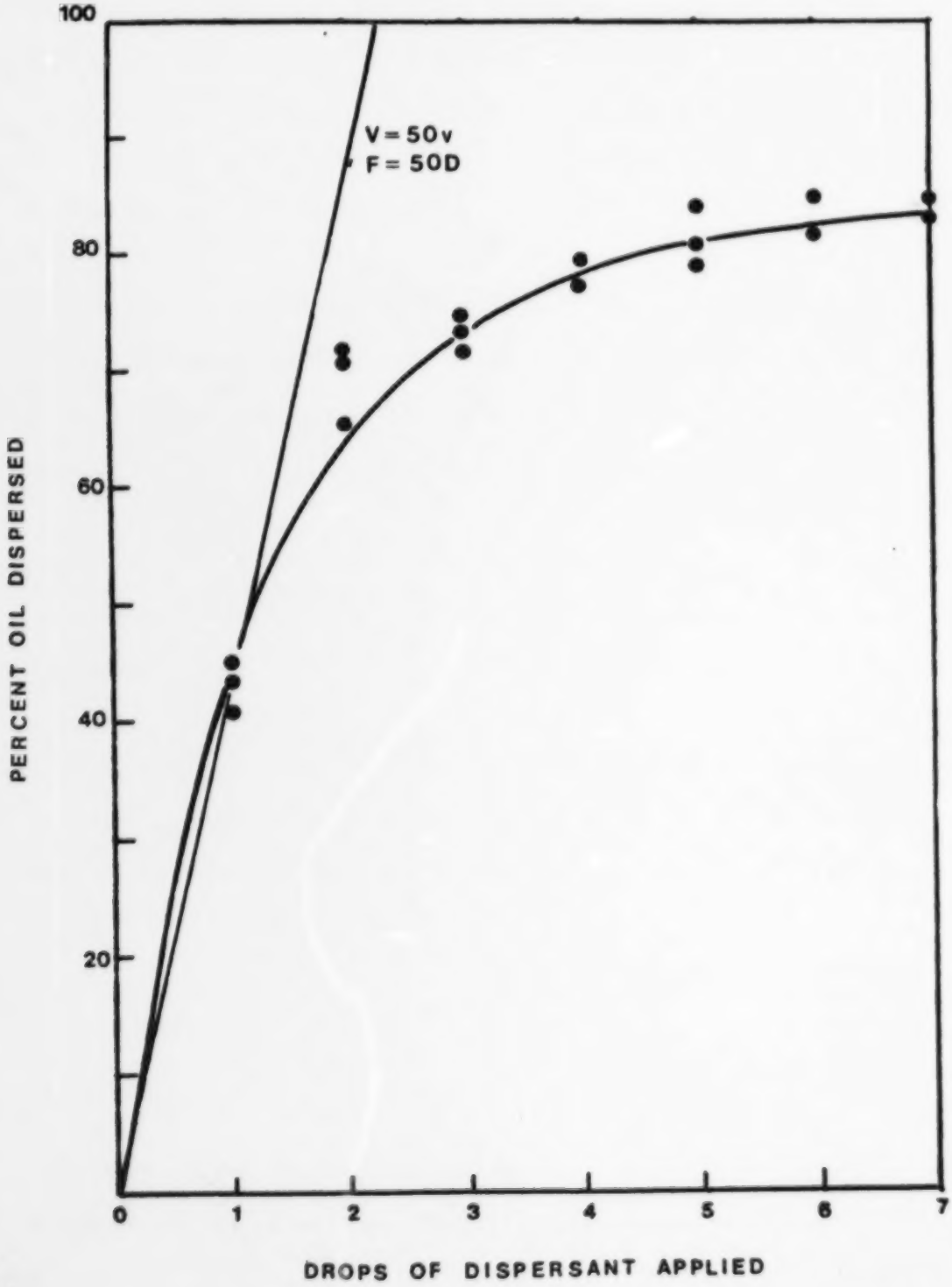


Figure 4.7: Double Tube Dispersion of Fuel Oil Mixture with Corexit 9527

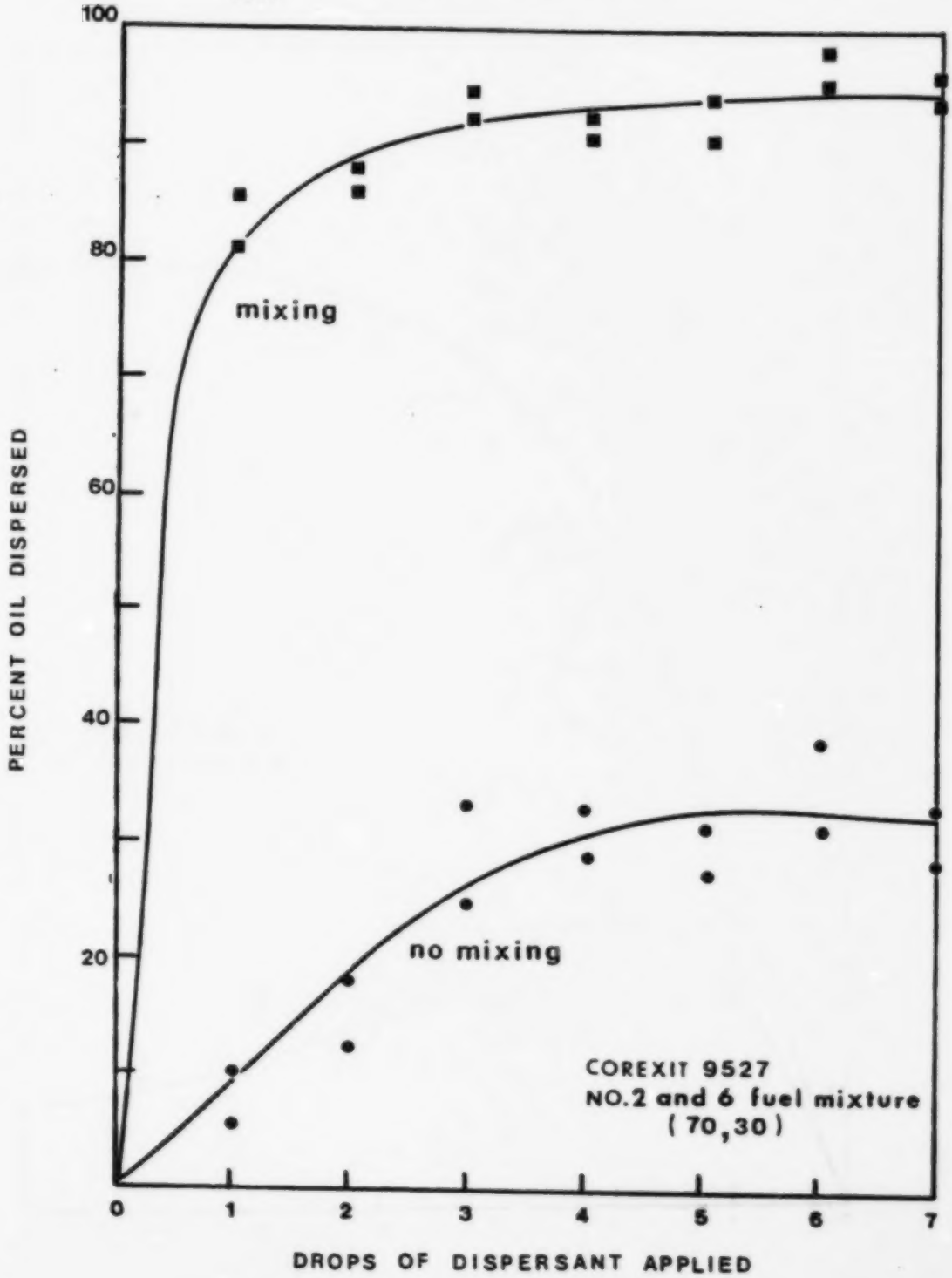


Figure 4.8: Double Tube System Disperion of Norman Wells Crude Oil with Corexit 9550.

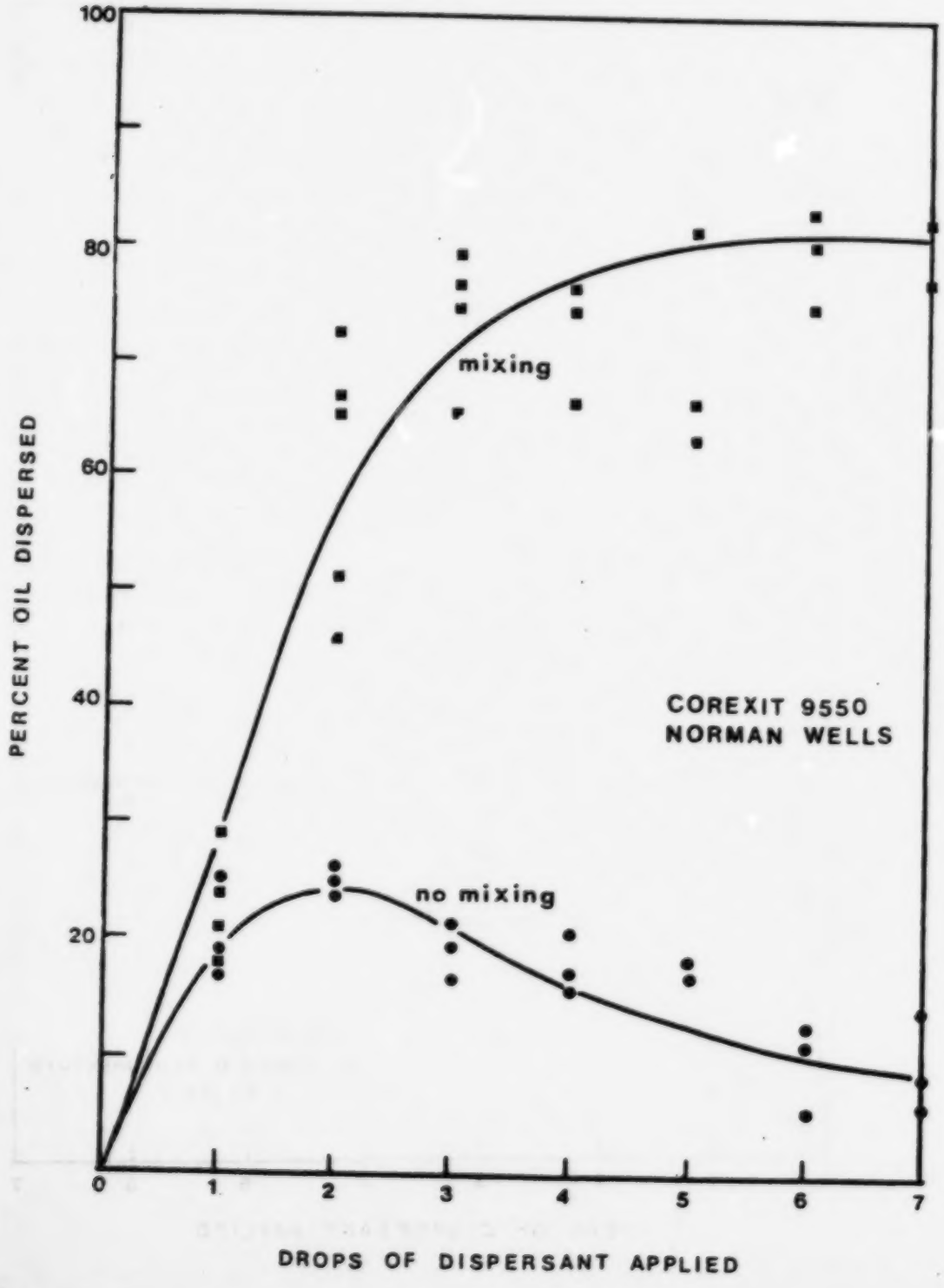


Figure 4.9: Double Tube System Dispersion of Fuel Oil Mixture with Corexit 9550.

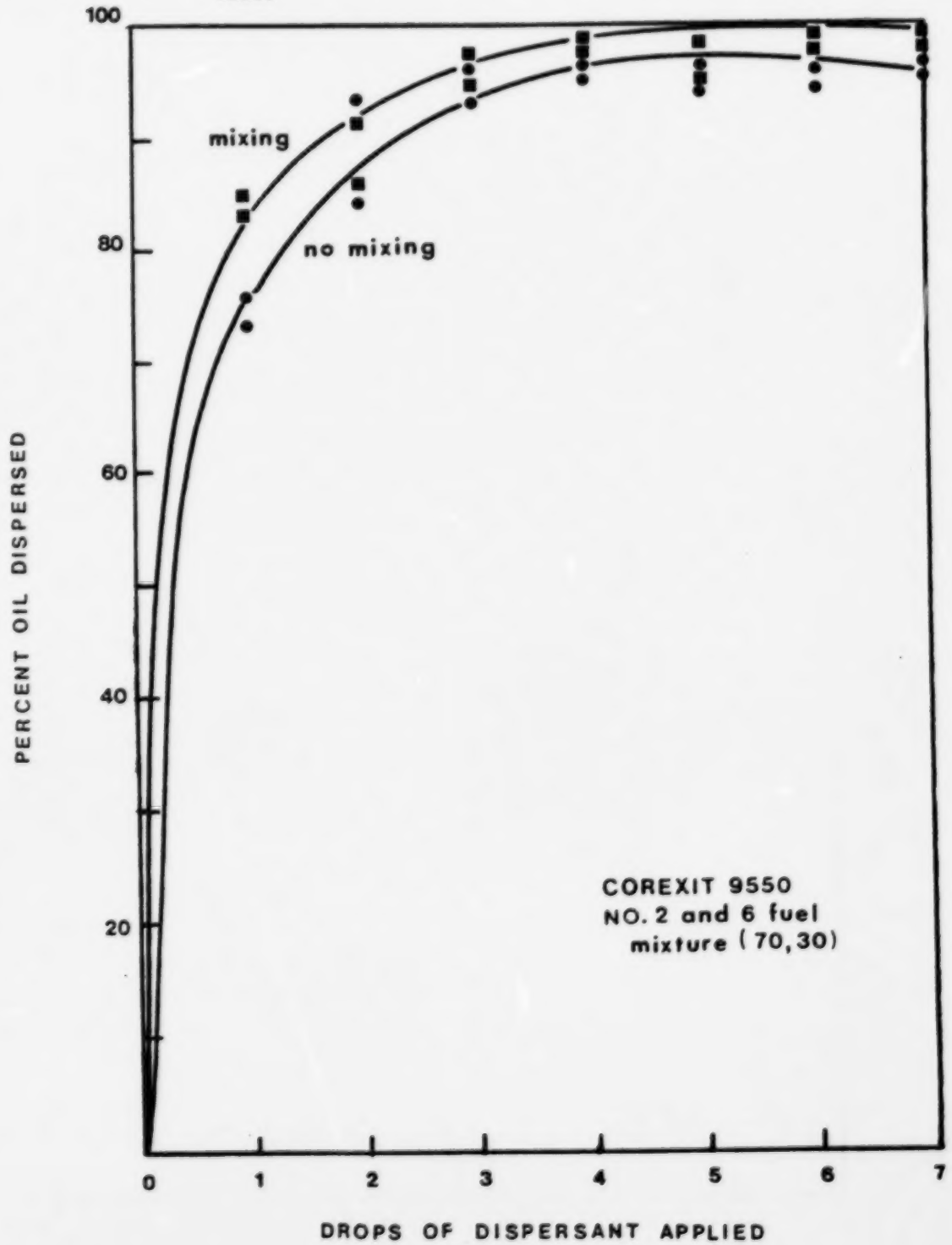


Figure 4.10: Double Tube System Dispersion of Norman Wells Crude Oil with BP MA700.

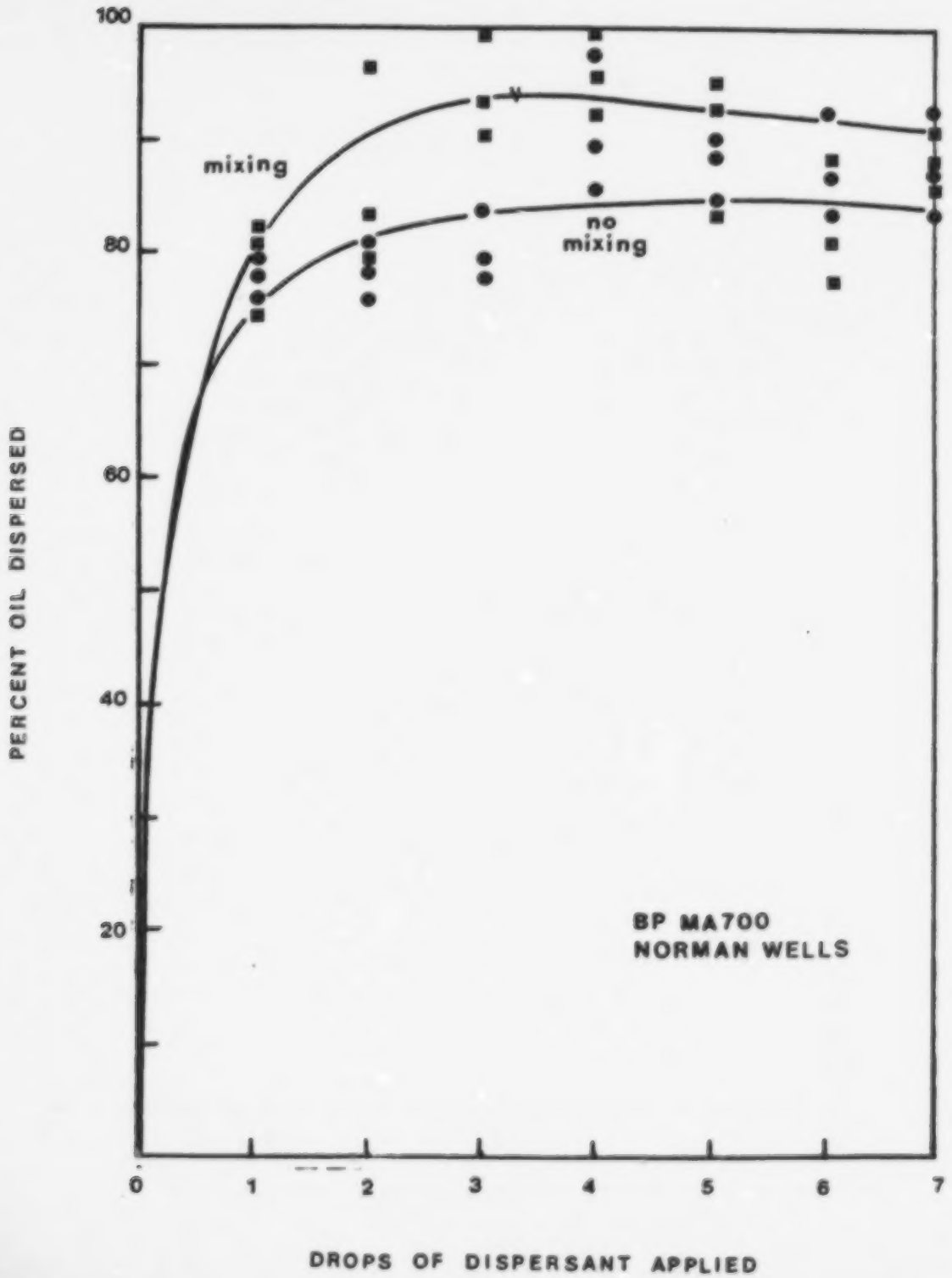
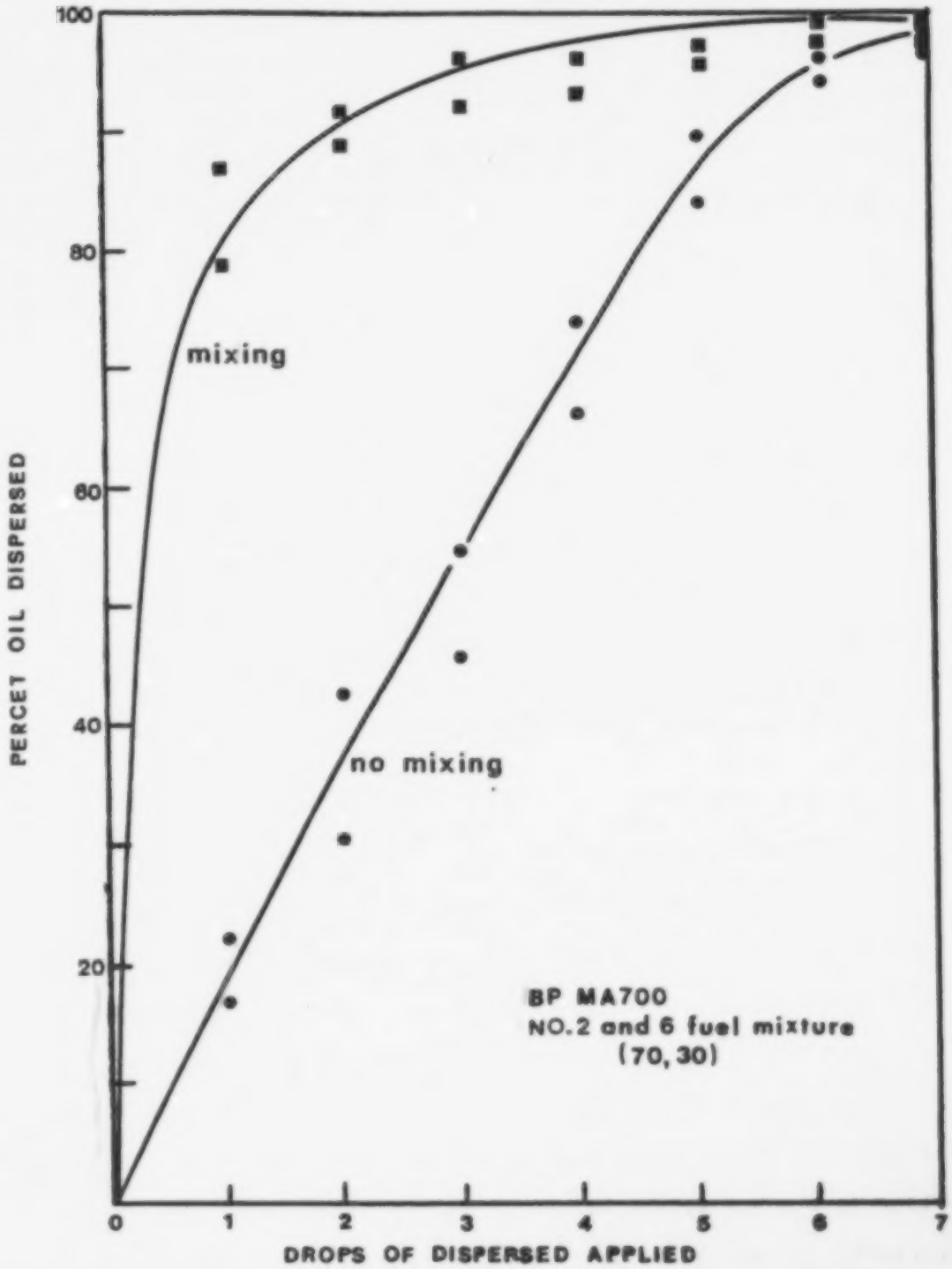


Figure 4.11: Double Tube System Dispersion of Fuel Oil Mixture with BP MA700.



It appears that the dispersants become quite ineffective in this test when the oil thins below 0.01 cm. Now the dispersant drop diameter in these tests is quite large (0.26 cm) the volume being 0.01 cm3. Thus at the "limiting" thickness of 0.01 cm corresponding to 70% dispersion, the dispersant drop is 52 times larger than the oil film is thick.

Recalling the discussion earlier, it appears that the dispersant drops of 0.01 cm^3 have the capability (for Corexit 9527 and Norman Wells crude oil) of dispersing 0.5 cm^3 of oil, which for the initial slick of 0.036 cm covers an area of 14 cm^2 or a 3.7 cm square, i.e. a M value of 3.7/0.26 or 14. Here M is the equivalent access ratio. The implication is that the dispersant drop can access oil located up to 7 diameters around it. But when the slick thins to 0.01 cm the drop is required to access oil over 50 cm^2 or a square of side 7 cm or a M of 27. This is apparently too large an area to access or influence.

It seems likely that when smaller drops of dispersant are used the same general principle applies.

Examination of the data indicates that M of 20 is approximately the limit for these test conditions. We can postulate that this "access area" is controlled by the ability of the dispersant to spread, thus influencing a certain area.

An explanation of the phenomenon is offered as follows. The dispersant has the capability of dispersing 50 times its volume of oil provided that a sufficient volume of oil is accessible. The dispersant can access an oil volume corresponding to the area under a circle M or here 20 times the drop diameter. For a drop of volume

0.01 cm^3 this area is 22 cm^2. The dispersant then disperses the smaller of two potential oil volumes. For a thick slick the "performance" is limiting i.e. the factor of 50 controls. For thin slicks "access" controls. This is illustrated below in Table 4.2 which follows the sequential dispersion of Norman Wells crude oil by Corexit 9527 without mixing by 0.01 cm^3 drops with a factor of 50 and an accessible area of 22 cm^2. The results are also plotted on Figure 4.5. Mixing apparently increases the performance factor to 80 as a result of the availability of more energy.

There are thus two dispersion regimes, performance-limited and access-limited. When dispersant is applied the process may be in either regime entirely or it may pass from performance - limited to the access-limited regime. We use this later as the basis for a mathematical model of the dispersion process.

Table 4.2 Sequential Dispersion Process.

Drop No.	Oil Volume	Oil thickness	Potential Oil Dispersed Performance(1)	Access(2)	Percent Dispersed
1	2.4	.036	(0.50)	0.79	21
2	1.9	.028	(0.50)	0.61	42
3	1.4	.021	0.50	(0.46)	63
4	0.94	.014	0.50	(0.31)	74
5	0.63	.0094	0.50	(0.21)	82
6	0.42	.0063	0.50	(0.14)	88
7	0.28	.0042	0.50	(0.09)	92

(1) Potential Volume of oil dispersed by a 0.01 cm3 dispersant drop based on its performance of dispersing 50 volumes oil per volume of dispersant.

(2) Potential volume of oil dispersed by a 0.01 cm^3 drop assuming that it can access an area of 22 cm^2.

The lower values in parentheses are selected.

4.3 Effect of Oil Slick Thickness in the Hoop Apparatus.

The Double Tube results presented earlier suggest that effectiveness falls when the oil slick thins, due presumably to poor accessibility or mixing. Some hoop apparatus tests were conducted to investigate this using Norman Wells oil and Corexit 9527. The results are given below in Table 4.3. The percentage dispersed (F) and the volume of oil dispersed per unit volume of dispersant (X) are given.

Table 4.3 Effect of Slick Thickness.

Volume of oil	Volume of dispersant	DOR	Oil thickness	F	X
cm3	cm3		mm	%	
2	.172	1/12	0.3	75	8.7
10	.191	1/52	1.2	35	18
50	.174	1/287	2.7	20	57
100	.183	1/546	3.1	12.5	68
50	.964	1/52	2.7	60	31

Clearly as the slick thins X falls, although the effectiveness rises. The two tests at a DOR of 1/52 show that X is larger when the slick is thicker. These results are consistent with the Double Tube results and suggest that for thick slicks the effectiveness is controlled primarily by the volume of dispersant, i.e. X is relatively constant and here appears to lie in the range 30 to 70. As the slick thins, access becomes a problem and X falls. The use of X or DOR as a predictor for effectiveness is thus potentially misleading unless slick thickness is taken into account. The best performance is obtained when dispersant is added to thick slicks. The Double Tube and Hoop systems

thus yield the same conclusion that slick thickness is a critically important parameter.

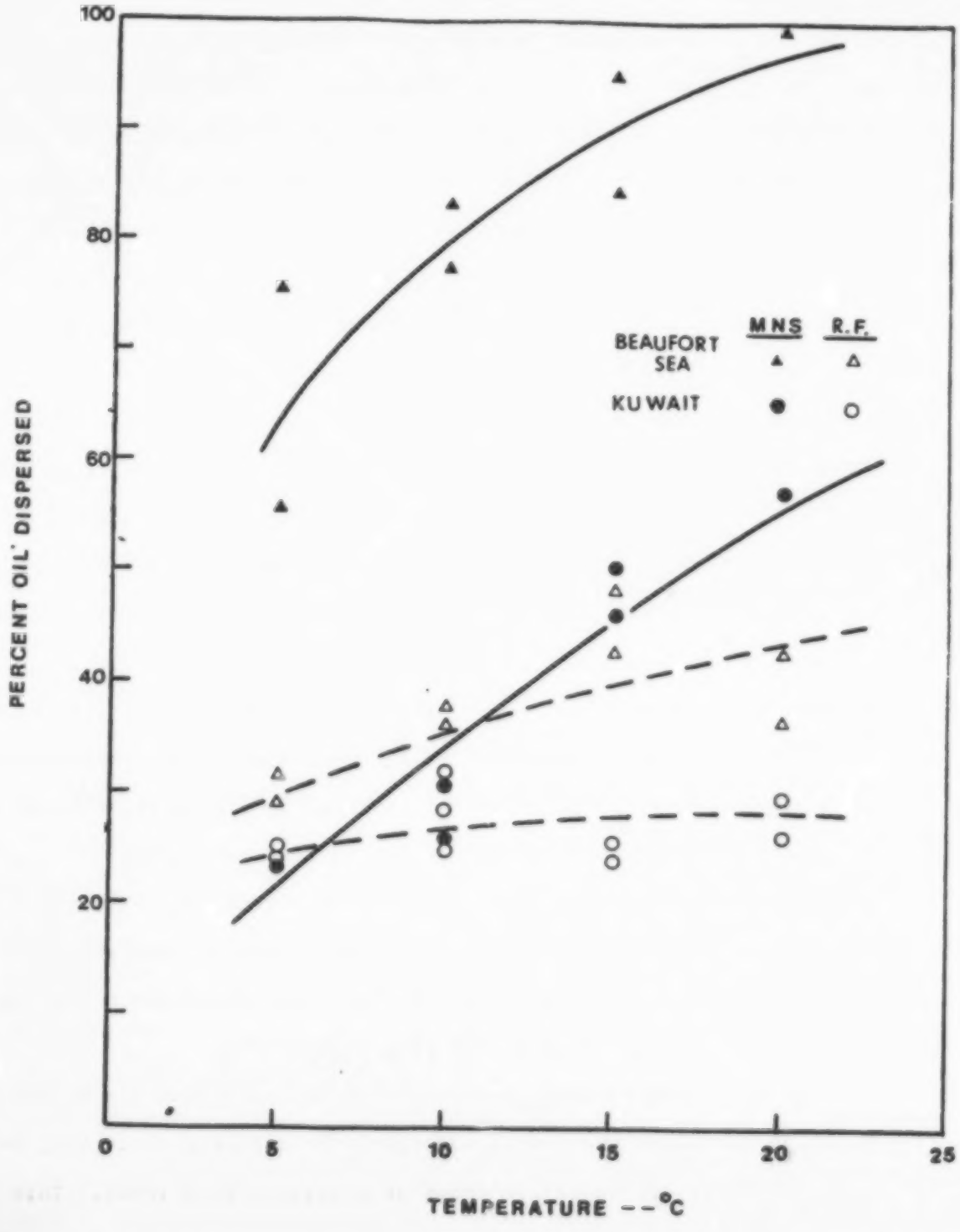
4.4 Effect of Temperature.

To illustrate the effect of temperature on dispersion a series of tests was conducted with Corexit 9527 on Beaufort Sea and Kuwait oils at 21 cm pressure drop using a D/0 ratio of 0.015. The results shown in Figure 4.12 show the trend for decreasing effectiveness at low temperatures. The MNS results are consistent with other results obtained in our laboratories in which over the temperature range 25 to 0 degrees C there is about a halving of effectiveness or a doubling of the dispersant dosage required to achieve a defined performance. The RF tests show less temperature dependence.

The "obvious" reason for this behaviour is the oil viscosity increase. The density changes are regarded as negligible, especially since it is the relative oil-water density which is significant and both oil and water densities change. Less obvious is why viscosity influences effectiveness. It is observed that oils of viscosity 500 m.Pa.s are often as easily dispersable as those of 10 m.Pa.s thus it appears that viscosity is not a particularly important parameter, at least in the range 10 to 1000 m.Pa.s. A change in temperature from 25 to 0 degrees C may cause a 10 fold increase in viscosity, thus it is tempting to postulate a relationship of effectiveness being proportional to viscosity to a power of approximately -0.3, but this does not seem to apply between oils since an oil of high inherent viscosity (e.g. 1000) should be very much less dispersable than one of low inherent viscosity (e.g. 10) by a factor of 4.

It is suspected that an increase in viscosity has two effects. First it increases the energy necessary for oil drop formation, thus it tends to result in larger drops at a given energy level. This

Figure 4.12: Effect of Temperature on Dispersability of Beaufort Sea and Kuwait Crude Oils



effect becomes dominant above 5000 m.Pa.s. Second, it alters the oil dispersant mixing process, possibly improving it for light oils by retarding oil penetration through the oil into the water.

As a further illustration of the effect of viscosity, a set of 11 crude oils and fuel oils with viscosities varying from 3 to 8000 m.Pa.s were tested with three dispersants (Corexit 9527, Corexit 9550 and BP MA700) using the MNS and RF systems. The results are given in Figure 4.13 to 4.15 as plots of percent oil dispersed versus viscosity. In the range of 3 to 1000 m.Pa.s there was no distinct trend for effectiveness to fall in the RF test, i.e. the "lines" are vertical. For the MNS there is a tendency for a loss in effectiveness but it is slight. An interpretation of this is that the RF test is essentially measuring droplet rising velocity or the group

(diameter squared)(water-oil density difference)

It is possible that the effect of an increase in viscosity is to increase oil drop diameter, but there is a decrease in density difference which offsets that effect.

The MNS test is primarily measuring the oil slick break-up rather than the emulsion stability. Break-up is a slight function of viscosity in the range 3 to 1000 m.Pa.s.

Temperature reduction may also have the effects of causing "precipitation" of waxes which retard oil-dispersant mixing and reduce diffusive mixing of the dispersant into the oil. This is particularly likely close to the pour point.

It is apparent that there are several coincident and competing processes which are difficult to study in isolation. Perhaps the overall conclusion is that an effectiveness temperature coefficient of

Figure 4.13: Dependence of Dispersability on Viscosity Using Corexit 9527.

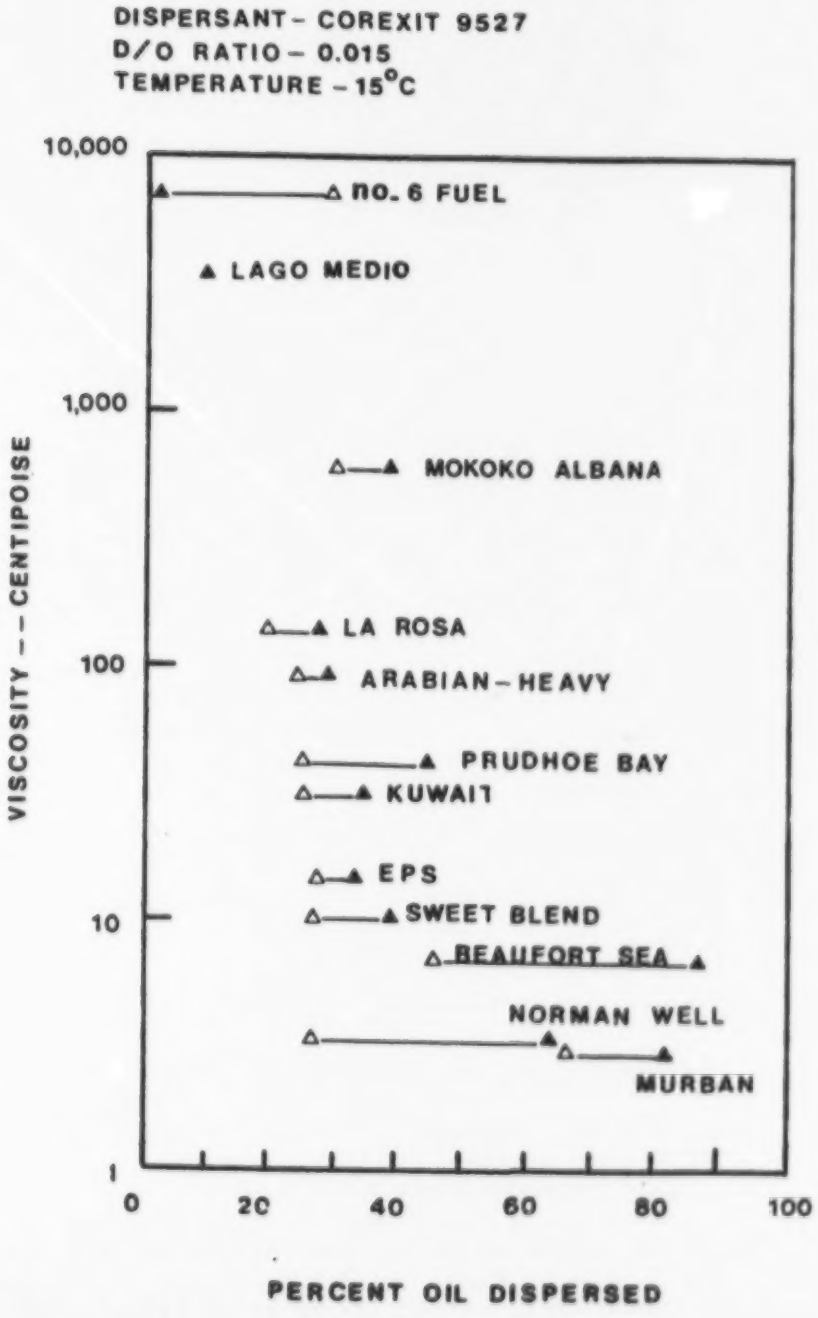


Figure 4.14: Dependence of Dispersability on Viscosity Using Corexit 9550

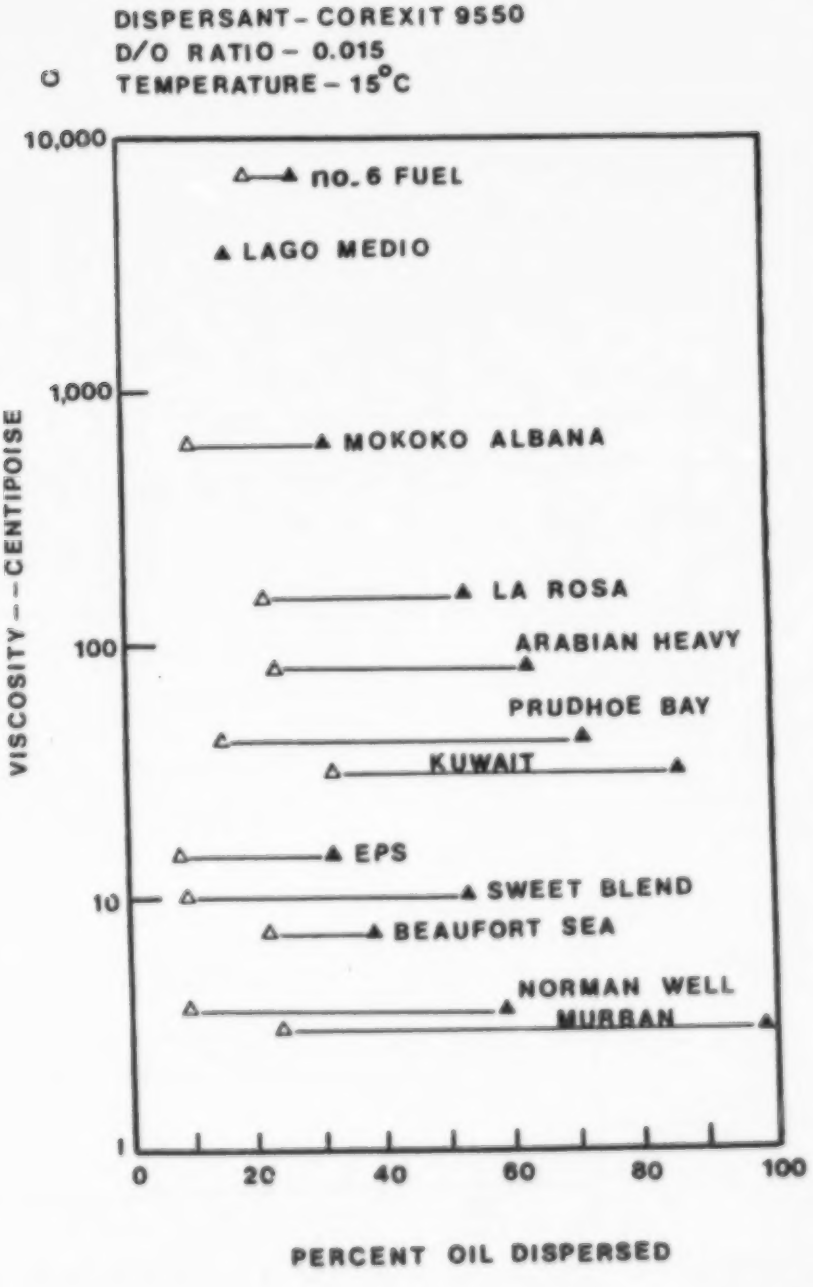
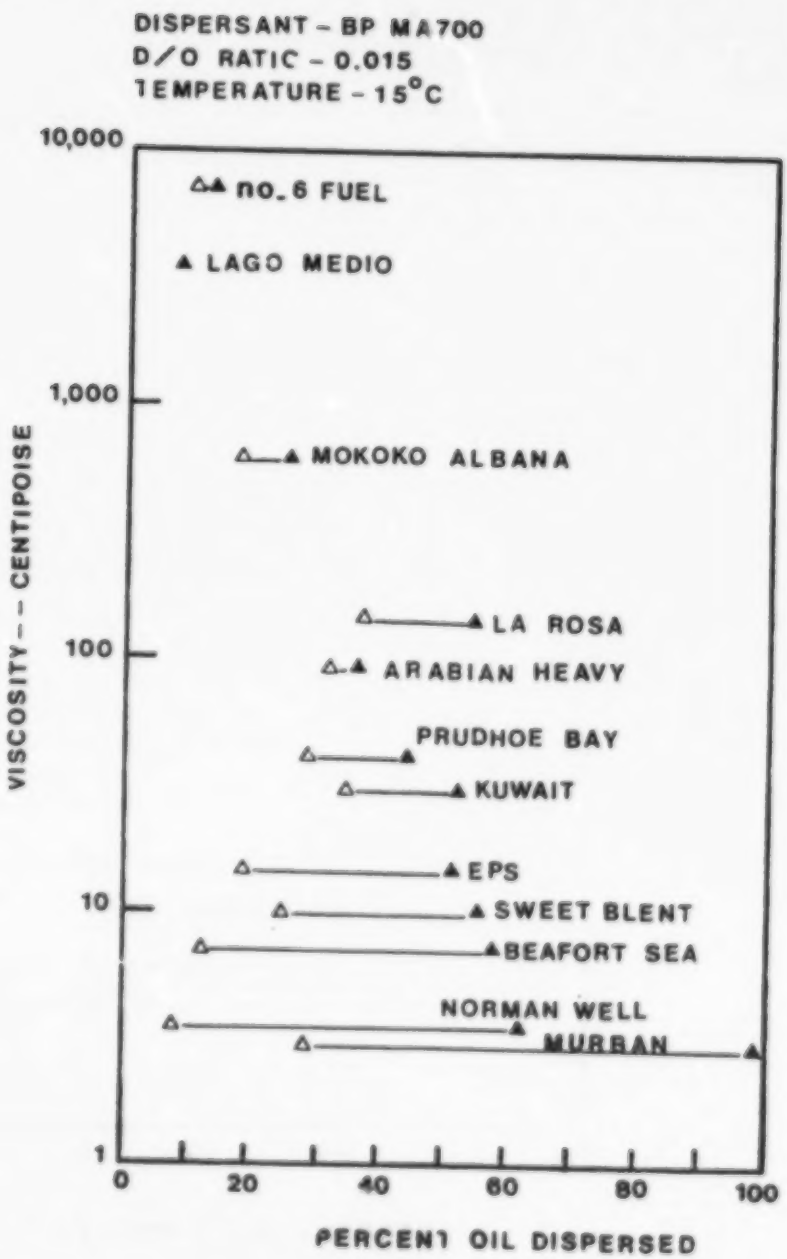


Figure 4.15: Dependence of Dispersability on Viscosity using BP MA700



a factor of approximately 2,often applies between 0 and 25 degrees C, but each oil-dispersant combination should be studied to obtain its specific coefficient. This "rule" is likely to break down at high viscosity and close to the pour point temperature.

From the viewpoint of dispersion of oil spills under Arctic conditions, which is a primary concern of the sponsors of this project, it can be concluded that dispersion is likely to require more dispersant under these cold conditions but the extra amount is unlikely to be large except when the oils are unusually viscous, close to their pour point or waxy. There is no inherent reason to suggest that cold climate dispersion is significantly less feasible than temperate dispersion. It is noteworthy that water temperatures in the Arctic are constrained to above-freezing conditions and are thus often considerably higher than air temperatures. An oil slick is in intimate contact with the water and is likely to be at the ocean temperature. The dispersant, if applied aerially, could however be at a much lower temperature.

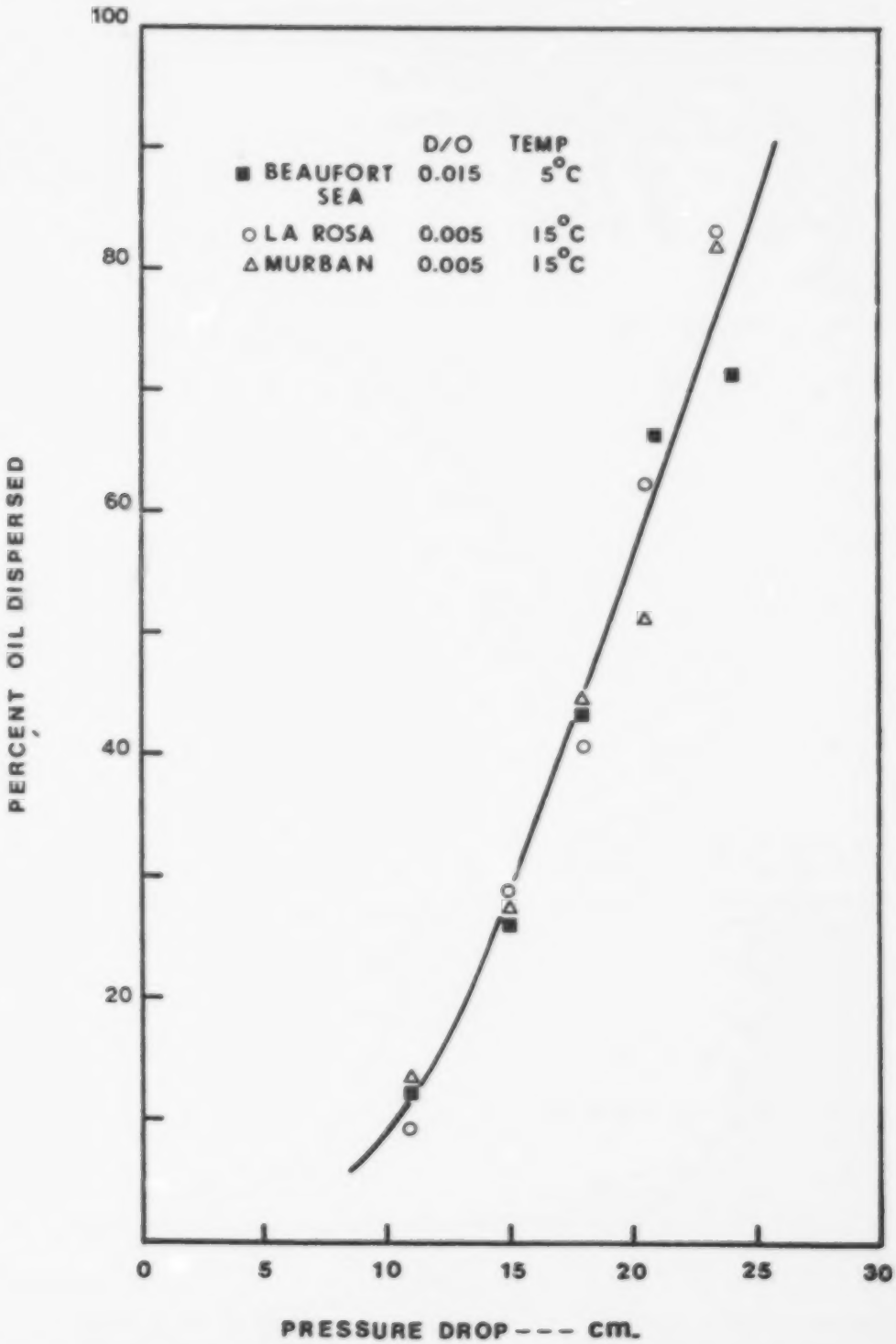
4.5 Effect of Turbulence.

Figure 4.16 gives test results using the MNS system at various turbulence levels as indicated by orifice plate pressure drop. It is clear that turbulence has a profound effect. It is not possible to vary the turbulence in the RF test.

The explanation of this effect seems straightforward. The oil water interfacial tension is usually about 20 mN/m or equivalently 20 mJ/m^2, thus to create $1m^2$ of new surface area requires 20 mJ of energy at the right place and with the right length scale or availability. Addition of dispersant considerably reduces the interfacial energy to less than 1 mJ /m2 thus much less energy is required to create surface area and the available energy is able to disperse more oil. Conceptually, the same phenomenon appears to be occurring as with the effect of temperature on chemical reaction when the activation energy is reduced and hitherto slow reactions are speeded up.

Confirmation of the importance of surface area generation as a parameter can be found in the results of Lewis et. al. (1985) who measured the areas formed at DOR values from 1/100 to 1/16.7 in the RF test. They found that the area of oil surface generated per unit volume of dispersant was relatively constant (i.e. it varied only by maximum factors of 2.8, 1.2 and 1.8 for three dispersants). At a given energy level a dispersant thus appears to be able to generate a certain interfacial area. Increasing the amount of dispersant tends to generate more area but with the same diameter, thus more oil is dispersed, i.e. X is fairly constant. Increasing the energy level increases the area formed but it also decreases the median drop diameter. More smaller drops are formed thus the effectiveness rises

Figure 4.16: Effect of Turbulence in the MNS System on Dispersability



because a greater fraction of the dispersed oil is below the critical diameter for resurfacing.

But this critical diameter for resurfacing also depends on the water column turbulence level thus there are two complementary effects of energy; the generation of small drops, and the ability to keep these drops in suspension. If a given volume of oil is dispersed then the drop diameter DP is inversely proportional to the area created and thus to the energy dissipated. The problem is to estimate the fraction which is smaller than some critical diameter DC, the magnitude of which depends on the water column velocities which are probably related to the wind velocity, or in the MNS system to the pressure drop.

A simple quantitative treatment is to assume a Weibull type of distribution of oil drop diameter and postulate that the fraction of oil drops formed which have a diameter less than some critical diameter DC is given by

$$1 - \exp(-DC/DP)$$

where DP is a diameter characteristic of the population and is here postulated to be inversely proportional to energy level. DC is a function of the oil density and the turbulence level in the water as controlled by the test conditions or wind speed at sea.

The MNS test results given earlier in Figure 4.16 are well correlated by an expression of the type

$$F = 1 - \exp(- P2/444)$$

which we can interpret as being a proportionality between DC and energy expressed as pressure drop P, combined with an inverse relationship between DP and energy. An increase in energy or P causes DC to increase and DP to fall and F to rise.

The hoop test results of Lewis et. al. (1985) suggest that when the energy level is increased from 100 to 200 RPM DC remains fairly constant but the diameter DP falls from 37 to 19 (um) for one dispersant, and 63 to 37.5 for another, almost a factor of two. A third showed little decrease in DP (69 to 60) but the effectiveness rose from 15% to 89%. In all cases the diameter distribution moved towards smaller diameters but in the third case a mean diameter of 69 appears to correspond to a spectrum with most drops above DC, thus the shift in spectrum has little effect on the measured mean diameter.

When developing a model of dispersion which is applicable to oceanic and laboratory conditions it appears that it is necessary to define two energies (i) the dispersion energy and (ii) the water column suspension or turbulence energy. At sea these energies are intimately coupled and could possibly be expressed in terms of wind speed or sea state. In the laboratory tests they may differ. Using the data of Lewis et. al. (1984) and Mackay et. al. (1984) and the data generated here it appears that the following is a reasonable ranking of energy levels

Table 4.4 Tentative Energy Rankings.

	Dispersion	Suspension
	Hoop 200 RPM	MNS OTC 30
Highest energy	MNS OTC 30	MNS OTC 17
	Hoop 150 RPM	Hoop 200 RPM
	RF	Hoop 150 RPM
	MNS OTC 17	Hoop 100 RPM
Lowest energy	HOOP 100 RPM	RF

Here the MNS energy is expressed as the measured oxygen transfer coefficient (OTC) in cm/h. The key problem is to insert oceanic conditions into this table. It is suspected that the OTC may be a fairly good indicator of dispersion energy, thus the RF, hoop at 150 RPM and MNS at an OTC of 20 are typical of approximately 7 m/s sea conditions. The suspension energies are less certain, but it is likely that the RF test has too low a suspension energy and the MNS too high a suspension energy to properly simulate oceanic conditions.

4.6 Effect of Salinity.

A series of tests was done at 15 deg C using Beaufort Sea crude oil and Corexit 9527, Corexit 9550 and BP NA700 (DOR 0.015) with distilled water, Toronto tap water and 30 g/L seawater. The distilled and tap water results were identical. The salt water effectivenesses were higher especially for Corexit 9527 (29% vs 5%) with less marked increases for Corexit 9550 (9% vs 7%) and for BP NA700 (19% vs 10%). It is believed that the fresh water dissolves the surfactant and/or solvents more rapidly because of the lack of the "salting out" effect thus more dispersant is lost to the water column.

Under Arctic conditions this effect could be important if dispersant is applied to water containing appreciable amounts of ice melt water, or to river estuaries. When assessing the suitability of dispersants for use in variable salinity waters there is presently no alternative but to measure the magnitude of the salinity dependence of dispersion on a case by case basis. It is possible that there are interactions between oil type, dispersant type, salinity and temperature.

4.7 Oil-Dispersant Mixing.

In view of the obvious importance of the oil-dispersant mixing process some exploratory tests were done in which an attempt was made to observe and measure the rate at which a dispersant mixed with, or dissolved into crude oils. Various contacting systems were tried and finally a system was devised consisting of a long vertical tube filled with oil into which dispersant was added at the surface and the behaviour observed. Among the expected observations were the falling velocity (which is presumably a function of density difference) and the time for total dissolution (which is a function of mutual solubility or miscibility). It was hypothesized that a good dispersant would sink slowly and mix rapidly with the oil. A poor dispersant would tend to remain as a separate phase longer.

An 8 mm (i.d) x 120 cm Pyrex tube enclosed at one end and marked in cm was filled with a crude oil to a height of 115 cm (about 57.5 mL). 1.00 g of dispersant Corexit 9527 containing a fluorescent dye was rapidly added on the crude oil column and the rate of descent was viewed under long wave-length UV illumination and marked by a stop-watch.

Three crude oils, Norman Wells, La Rosa and Mokoko Albana were examined. In general, immediately after the dispersant was added, there was mixing to a depth of 1 cm on the top of the crude oil column, where the fluorescent dye of the dispersant could be seen several minutes after addition in the case of Norman Wells and Mokoko Albana crudes. In the case of La Rosa, fluorescent spots took 2-3 minutes to appear after addition. "Streamers" of this dispersant/crude oil mixture then started to descend on the inner surface of the column.

Towards the end of its descent, lateral mixing could be seen so that finally only the tip of the "streamer" was left.

Plots were prepared of descent distance versus time. After 20 minutes the dispersant had fallen 32 cm in the low density Norman Wells oil, 1.5 cm in the denser La Rosa oil, and 1.5 cm in the dense Mokoko Albana oil. The results are summarized in Table 4.5.

The falling velocity is clearly a function of oil viscosity and oil-dispersant density difference, thus the dispersant fell rapidly through the Norman Wells oil and had the potential to pass through without mixing. This oil is easy to disperse because of its low viscosity. The La Rosa and Mokoko oils are interesting to compare because the latter has a higher viscosity but is more easily dispersed. It mixes more rapidly with the dispersant thus it may retain more of the dispersant following application.

This exploratory study has shown that there are profound differences between oils with respect to their mixing characteristics with dispersants. There is a possibility that a test could be devised, similar to that described above, which would provide information about (i) the likely tendencies for dispersants to penetrate oil rapidly and induce herding and (ii) the ease of mixing. Such a test would not measure effectiveness but would provide an insight into one of the factors which controls effectiveness.

Table 4.5 Physical Constants of Crude Oils Analyzed.

	Norman Wells	La Rosa	Mokoko Albana
Composition (% mass)			
Asphaltenes	1	9	2
Saturated	89	68	78
Aromatics	8	20	16
Polar	2	3	4
Density (a) kg/m3	842	914	942
Viscosity (a) m.Pa.s	3.6	147	631
% Dispersed (b)	65	29	40
Descent of dispersant, cm	61.3	17.5	3
Time of descent	175 min	29 hr.	120 min
Time of complete mixing	185 min	>72 hr.	210 min

a. Measured at 15 deg.C

b. Measured with MNS apparatus, using Corexit 9527 and a dispersant/oil ratio of 0.015.

4.8 Herding.

It is frequently observed that dispersant drops induce herding of thin oil slicks. This can be readily observed in simple petri dish tests in which the dispersant drop can be seen to penetrate the oil film, and when a water-dispersant-air layer forms the low total surface energy of this configuration compared to the water-oil-air layer causes expansion of the dispersant area at the expense of the oil area. The net effect is to reduce the oil area considerably. If this occurs during dispersant application it could greatly reduce the interaction between dispersant and oil.

Some effort was devoted to studying this effect experimentally, it being hoped that it would be possible to determine some combination of oil film thickness and dispersant drop size that would characterize the onset of herding. This proved to be very difficult because no facilities existed for producing mono-dispersed (constant diameter) drops of the desired velocity nor are oil films easy to control. The results suggest that three regimes may exist, as a function of ratio of dispersant drop diameter to oil slick thickness (D/T ratio).

(i) At low D/T ratios the dispersant merely spreads over and mixes into the oil and will not induce herding

(ii) At high D/T ratios herding occurs

(iii) There is an intermediate range in which herding may or may not occur depending on the velocity of impact of the dispersant drop and the oil viscosity.

The transition D/T ratios could not be determined accurately but appear to lie in the range of 1 to 10.

It is noteworthy that the effect considered here is related to the

"access-limited" effect considered earlier and may be quantified by the ratio M.

From both prospectives (access and herding), the use of small dispersant drops is preferable. When developing a mathematical model it is thus desirable to include this effect. An attractive approach is to use the M ratio recognizing that it plays a dual role of defining access and herding. An "effective M" may then be deduced which characterises both phenomena. For example it may prove advantageous to correlate data with a lower M value than the 20 suggested earlier because of the herding effect. This is discussed later.

It is suggested that the herding phenomena is worthy of further experimental investigation.

5. DISCUSSION AND MATHEMATICAL MODEL.

5.1 The Dispersion Phenomena

The results obtained here and in other studies suggest that the following is the mechanism of dispersion.

First, the oil slick spreads unevenly into thick and thin or sheen slicks with the sheen usually having the larger area. The thick slick, however, contains most of the oil, possibly some 90%.

The dispersant is sprayed on to the oil in the form of droplets. If the oil slick is thick compared to the dispersant drop diameter the dispersant will tend to sink into the oil and mix or dissolve into it, but some may penetrate the slick and enter the water. This may cause oil herding and subsequent dispersant drops may land on the exposed water surface. This oil-dispersant dissolution process is apparently influenced by the chemical composition of the oil, particularly the wax or paraffinic content and the densities and viscosities of both fluids. It is very variable between oils. Effective mixing may be favoured by having small dispersant drops, a thick slick and approximately equal oil and dispersant viscosities and densities.

Migration of surfactant to the oil-water interface causes a reduction in interfacial tension or surface energy at that interface. The available energy from wind and waves or from artificial sources such as breaker boards causes disturbance of the interface and induces formation of oil drops with a spectrum of sizes. The volume median drop diameter may range from 10 to 200 um, a typical value for effective dispersion being 50 um. The more effective dispersants and high energy levels (i.e. high wind speeds or artificial agitation)

tend to create smaller drops. These drops diffuse into the top metre or two of the ocean and some resurface depending on the relative oil and water densities, the droplet diameter and the prevailing level of turbulence in the water.

A simple mathematical approach is to postulate that as a first approximation for relatively thick slicks in which dispersant-oil mixing is effective, 1 volume of dispersant has the potential to disperse X volumes of oil, where X depends on the dispersant, the oil, the prevailing energy level, temperature and the method by which the dispersant is applied. X is higher when the oil and dispersant are premixed thus it contains an "efficiency of mixing" component. For a good dispersant a typical value of X is 50.

We postulate that there is a transition or boundary oil thickness below which the mechanism changes. Herding becomes more likely and the drop of dispersant is unable to disperse X volumes of oil because it can not "access" sufficient oil. We postulate that it can access a circle of area M times its diameter, where M is likely to lie in the range 5 to 20. Such thin or sheen slicks are usually overdosed with dispersant, whereas the thick slicks are underdosed.

In summary, dispersion may occur in two regimes, a "performance limited" regime which generally applies to thick slicks, and an "access-limited" regime which generally applies to sheen. This was illustrated earlier in the discussion of the Double Tube results.

Once dispersed, the oil drops diffuse under the influence of turbulent eddies with some resurfacing. This resurfacing tendency has been discussed by Wilson et. al. (1985) who, using Leibovich's (1975) analysis, derived a simple expression for the resurfacing rate

constant Kr as

$$Kr = U/(Y(1+V/U))$$

where U is the oil droplet Stokes' Law rising velocity, Y is the depth of dispersion and J is a turbulent velocity correlated as

$$J = 0.00043\ W^2/Y$$

where W is wind speed (m/s). The Stokes Law velocity is given by

$$U = Z^2(Rw-Ro)g/18u$$

where Z is the oil drop diameter, Ro is the oil density, Rw is the water density, g the gravitational constant and u the water viscosity.

A spectrum of oil drop diameters is created characterized by a population volumetric mean diameter DP. Now for a given observation time (To) (say 30 minutes after dispersion) there is a critical oil drop diameter DC above which most oil will resurface and below which most oil remains submerged. DC can be estimated as the value which gives the group KrTo a value of approximately unity. The fraction of the oil which resurfaces can then be estimated at To and other times if an oil drop diameter spectrum is assumed or is measured.

If DP greatly exceeds DC (as may occur under quiescent conditions or for an ineffective dispersant) most oil resurfaces. If DC exceeds DP most oil remains submerged.

As time progresses the dispersion depth Y increases from an initial value of a metre or two (or the wave height) to some 10 m. This has been described mathematically by Mackay et. al. (1982) who suggested that a typical vertical diffusivity Dv was 0.013 m^2/s. Under unsteady state diffusion conditions a penetration distance is expected of magnitude Dv.To. Thus at 30 minutes a distance Y of approximately 5 m is expected.

It has been suggested by Johansen (1985) that the sheen formed adjacent to the dispersed slick is largely created by resurfacing of dispersed oil which has become displaced horizontally (by wind drift) from the thick slick. This may be the primary cause of the observed increase in dispersed slick area rather than enhanced surface spreading. This sheen is probably subject to more rapid natural dispersion, and it may contain remnants of the dispersant which further enhance dispersion. Addition of chemical dispersant may thus enhance delayed dispersion and it is unwise to pronounce a dispersant application as being ineffective from only short term observations.

5.2 Mathematical Model

Based on the previous discussion we propose the following model which applies primarily to dispersion of an oil slick at sea, but which can also be applied to a laboratory test. It is hoped that it may ultimately be "calibrated" by laboratory tests and thus used in a predictive mode for oceanic spills.

First it is necessary to define the thick and sheen areas. We assume that the total area is given, as is the fraction of the area occupied by the thick slick (typically 20%), the total spill volume and the sheen thickness (typically 10 um). This enables the area, volume and thickness of the thick and sheen slicks to be determined.

Second, the total dispersant volume applied is defined. It is customary to try to apply more dispersant to the thick slick, thus a facility should be included to define the fraction applied to the thick slick. A dispersant drop diameter (typically 400 um) is defined, thus the number of drops applied, the number density, inter-drop spacing and the dosage (L/ha) can be deduced for both thick slick and sheen.

This is illustrated in Table 5.1 for a hypothetical slick of 20 m^3 on to which 1 m^3 of dispersant is applied (DOR 1/20). 20% of the slick area is thick and 30% of the dispersant is applied to this area. It is interesting to note that the DOR is 1/64 for the thick slick and 1/1.14 for the sheen, i.e. severe under-dosing and over-dosing occurs. This is regarded as a primary cause of poor oceanic dispersion.

Table 5.1 Dispersant Application to Non Uniform Slick.

	THICK	SHEEN	TOTAL
Slick Area (m^2)	20000	80000	(100000)
Fractional Area	(0.2)	0.8	1.0
Slick Volume (m^3)	19.2	.8	(20)
Slick Thickness (mm)	.96	(.01)	.2
Dispersant Applied (m^3)	.3	.7	(1)
Dispersant Fractions Applied	.3	.7	1.0
Oil to Dispersant Ratio	64	1.14	20
Number of Drops (Millions)	71656	167197	238853
Drops per square cm	358	209	239
Drop Spacing (cm)	.053	.069	.065
Dispersant Dosage (L/ha)	150	87.5	100

Data in parentheses ( ) are supplied as input, all other values are calculated.

It is now necessary to obtain an expression for fraction of oil dispersed as a function of dispersant dosage. We propose two regimes.

In a "performance" limited regime the volume of oil dispersed is simply X times the volume of dispersant applied where X depends on the oil, dispersant and energy level. The oil volume remaining Vr is thus

$$Vr = Vo - X.v$$

where Vo is the initial oil volume and v is the dispersant volume. This regime applies until a transition or boundary thickness is reached.

In the "access" limited regime the process of dispersion of the oil of volume V is first order of the form

$$dV/dn = -[3.14(M.D)^2 T/4]$$

where n is the number of dispersant drops, D is the dispersant drop diameter, M is the performance ratio and T is the oil thickness, thus the term on the right is the volume of oil accessible to each dispersant drop. This is consistent with the results discussed earlier in Section 4.2 in which the term on the right is $22T\ cm^3$. Now n is related to the dispersant volume by

$$n = v/(3.14D^3/6)$$

Substituting gives

$$dV/dv = -1.5\ M^2T/D$$

But as dispersion occurs the oil thickness T falls the relationship being

$$T = V/A$$

where A is area. Thus

$$dV/V = -1.5\ M^2dv/A.D$$

$$\text{or } Vr = VO \exp(-1.5\ M^2.v/A.D)$$

Now the "performance" regime differential equation can be written as

$$dV/V = - Xdv/V$$

The two differential equations for dV/V become equal when

$$1.5\ M^2 dv/A.D = Xdv/V$$

$$\text{or } V/A = Tb = XD/1.5M^2$$

Here Tb is the transition or boundary thickness between regimes. When the thickness T exceeds Tb the "performance" regime applies and when Tb exceeds T the "access" regime applies.

The general equation for both regimes is thus

$$Vr = (Vo - X.vp)\ \exp\ (-1.5\ M^2.va/A.D)$$

where vp is the dispersant used in the performance regime and va is the dispersant used in the access regime. They must add to give the total amount of dispersant v

$$\text{i.e. } vp + va = v$$

When calculating the extent of dispersion it is thus necessary to assign values to va and vp.

If the slick thickness is less than Tb, then dispersion is limited by access only, vd is zero and va is v.

If Xv, the volume of oil potentially dispersable in the performance regime is less than the volume of oil available for dispersion in the performance regime (Vo - ATb) then dispersion is limited by performance only, va is zero and vp is v.

If Xv exceeds (Vo-ATb) then both regimes apply, vp is then estimated as (Vo - A.Tb)/X and va is (v - vp).

In practice the general equation can be written

$$Vr = (Vo - X.vp)\exp(-1.5M^2.(v - vp)/A.D)$$

and only vp need be defined. In the three cases it is zero, v,or in the dual regime as (Vo - A.Tb)/X.

Having calculated Vr, it is possible to calculate the amount dispersed (Vo - Vr) and the percent dispersed. A separate calculation is done for the thick and sheen slicks and the overall dispersion calculated.

The input variables describing the dispersant performance are

(1) dispersant drop diameter D.

(2) accessible oil ratio M

(3) potential dispersion ratio X

This latter ratio is a function of dispersion energy (e.g. wind speed), temperature and whether the dispersant is applied neat, in water solution or is premixed. It is attractive to relate X to the surface energy as expressed by wind speed, a simple relationship being

$$X = Xo(W/Wo)^2$$

where Xo is the value which applies at a base wind speed Wo m/s. We select 7 m/s as Wo. A similar equation can be invoked for temperature dependence causing X to fall linearly by a factor of two from 25 to 0 deg. C.

In a second calculation, the resurfacing characteristics can be defined by a balance between the Stokes' Law rising velocity and the turbulent eddy diffusivity in the form of a resurfacing rate constant. The input variables are the wind speed (or in the case of a laboratory test the equivalent wind speed) the oil drop volume median diameter, which we postulate is a function of dispersing energy, oil viscosity and dispersant performance. To minimize the input variables this latter quantity should be related to X, the performance ratio. At

this stage it is difficult to propose theoretically-based equations but for working purposes we postulate a relationship of the form

$$DP = (\text{constant})/X$$

where DP is the mean oil droplet diameter (um).

We postulate that oil drops are subject to a resurfacing rate constant of

$$Kr = (U/Y)/(1 + J/U)$$

where U is the Stokes' Law velocity, J is the suspension or turbulent velocity (given earlier as a function of wind speed) and Y is the mixing depth of perhaps 1 m. The effectiveness of dispersion is measured at some time To, thus a substantial fraction of the oil drops of critical rising velocity U will have resurfaced when KrTo is unity. We can thus calculate U by solving the quadratic equation

$$1 = (U.To/Y)/(1 + J/U)$$

From U we can calculate the corresponding critical oil drop diameter DC which will approximately half resurface during the time period To. If a simple Weibull distribution of oil drops is assumed then the fraction f of oil drops of diameter exceeding DC in a population of mean oil drop diameter DP is

$$f = \exp(-DC/DP)$$

This has the correct properties that when DP is small compared to DC the dispersant is effective, f approaches 0 and few drops exceed DC, thus few resurface. When DP is larger than DC, f approaches 1.0, most drops exceed DC, and most resurface thus effectiveness is reduced.

If an actual oil drop diameter spectrum was available it would be possible to fit the "true" Weibull distribution using the second parameter B

$$f = \exp\left\{-(\Phi C/DP)^{\beta}\right\}$$

The extent of resurfacing can be estimated, as can the effectiveness at the measuring time, the remaining oil slick thickness and the mean concentration in the water column to the defined depth. For an oceanic spill this depth Y can be allowed to be a function of time. Following the arguments of Lewis et. al. (1985) about the differences between the MNS, RF and hoop laboratory tests, we suggest that equivalent wind speeds be devised for each, but that separate dispersion and suspension wind speeds be defined. This is essential for the RF test in which suspension conditions are quiescent. It then becomes possible in principle to test an oil and dispersant in the laboratory using both MNS and RF tests, fit the data to the model, then use the model to predict oceanic behaviour. Obviously calibration is needed using the same oil-dispersant combinations at sea and in the laboratory but this is possible to some extent through the Norwegian studies. In future sea tests it is thus desirable to test the oil and dispersant combination in the laboratory as well as at sea and attempt to link them through the model. The critical variables are the dispersant dosage, the slick thicknesses and the parameters X and N.

In this study it has proved to be impossible to undertake the detailed model calibration that is desirable but a preliminary calibration has been done and the model tested against selected oceanic and laboratory tests. The results are presented in the next section. A copy of the computer program is given in **Appendix 1.**

5.3 ILLUSTRATION OF MODEL.

A copy of the model listing in BASIC is given in Appendix 1. It is applied here to several spill situations as follows

Norwegian 1984 spill W1 (Lichtenthaler and Dahling 1985).

This spill of 10 m^3 reached an area of 32200 m^2, had a sheen area of 86%, and was treated with 0.444 m^3 of dispersant. The thick slick possibly received 30% of the dispersant. The wind speed was 4.5 m/s and the temperature 12 deg. C. There was considerable dispersion with concentrations of 10 to 60 ppm in the top metre at the mean sampling time of 185 minutes.

Esso/U.K. North Sea 1982 Spill (Cormack 1983).

This spill of 20 m^3 of oil of density 890 kg/m^3 was treated with 2 m^3 of dispersant at 2.5 m/s and 11 deg. C. The area was about 350,000 m^2 of which 10% may have been thick. There was very little dispersion. The mean dispersant drop size was 400 um. Sampling was assumed to be after 60 minutes. Very little dispersion was observed.

Halifax 1983 Spills (Gill et. al. 1985).

These spills have also been described in several papers at the 1985 AMOP Conference. Three 2.5 m^3 spills of a light oil (820 kg/m^3) were treated with Corexit 9527, Corexit 9550 and BP MA700. The sea temperature was 18 deg. C, the wind speeds were respectively 7, 6 and 13 m/s, the effectivenesses 4%, 20% and 41% at the DORs of 1/27, 1/8 and 1/9. It is not clear what the spill areas were but it is estimated that there was in each case a thick slick of 10000 m^2 and a

sheen of 20,000 m^2. Sampling was taken to be at 30 minutes.

Dutch 1983 Spills. (Delvigne 1985).

Of the nine spills, three are suitable for analysis here, numbers 4, 6 and 9 in which 2 m^3 of Statfjord oil (density 852 kg/m^3) were treated with OSR5 dispersant at a DOR of 1/20. The No. 6 spill was of premixed oil and dispersant. The conditions were respectively, wind speed, 2, 8 and 7 m/s areas 70000, 50000 and 70000 m^2, temperatures 18, 18 and 15 deg. C and dispersion rates 2, 25 and 2 percent per hour.

New Jersey 1978 Spills (McAuliffe et. al. 1980).

These spills of 1.67 m^3 of La Rosa and Murban oils (densities 910 and 830 kg/m^3) were treated with 0.150 m^3 dispersant at 14 deg. C, 5 m/s and were sampled after 1 hour to give 50% and 100% dispersion. Areas were assumed to be 20000 m2.

Southern California 1979 Spills (McAuliffe et. al. 1981).

One spill of 3.18 m^3 of Prudhoe Bay oil (density 890 kg/m3) is considered in which treatment was with 0.120 m^3 of dispersant at 5 m/s, at an assumed 15 deg. C with an area of 22500 m^2. Dispersion was estimated to be 60%.

In a typical MNS test 10 cm^3 of oil (area 38 cm^2) treated with Corexit 9527 gives 50% dispersion at a DOR of 0.015, whereas in the RF test under similar conditions the effectiveness is 20%. In the RF test the volume of oil is 5 cm^3.

By trial and error the following wind speed (m/s) are assumed to

apply to these laboratory tests.

Test	Dispersion	Suspension
MNS	5	5
RF	4	0

It must be emphasised that in many cases it has been necessary to assume values for areas, temperatures, dispersant volumes and especially fractional areas of thick and sheen slicks and fractional dispersant dosages. Few reports give all the data required by this model. An implication for future experimental oil spills is that there should be a clear prior statement of data needs in order that the experimental results can be fully explcited in improving the model. Past "mistakes" of data acquisition are forgivable because no models existed to "demand" the data. This excuse no longer exists and future spills should be carefully planned with the model needs in mind.

The model was tested against these spills and adjustment made to the various parameters in an attempt to fit the one model to all conditions. The final results are given in Figures 5.1 to 5.13 which are self explanatory. Rather than tabulate all the input data, reference can be made to these figures for the input data which are asterisked.

It was found that a H value of 5 (Q in the computer program) was most satisfactory.

In most cases a dispersant such as Corexit 9527 was used and was assigned a X value of 50 at 7 m/s. The exceptions are Corexit 9550 at the Halifax trial and OSR5 in the Dutch trials.

The best estimate of oil drop diameter was obtained using the simple expression.

Figure 5.1: 5.15
NORWAY 1984 W1

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	9.723079	.27692	10 *
SLICK AREA (m2)	4508	27692	32200 *
SLICK THICKNESS (mm)	2.15685	.01	.310559
FRACTIONAL AREAS	.14 *	.86	
DISPERSANT APPLIED (m3)	.1332	.3108	.444 *
DISPERSANT FRACTIONS APPLIED	.3 *	.7	
OIL TO DISPERSANT RATIO	72.9961	.8909909	22.52252
NUMBER OF DROPS (MILLIONS)	3976.912	9279.459	13256.37
DROPS PER SQUARE CM	88.21897	33.50953	41.16886
DROP SPACING (mm)	1.06468	1.727491	1.558532
DISPERSANT DOSAGE (L/ha)	295.4747	112.2346	137.8882

DISPERSANT DROP DIAM (um)	400 *
POTENTIAL DISPERSION RATIO	26.42857
POTNTL DISPSN RATIO AT 7 m/s	50 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	850 *
TEMPERATURE (deg C)	12 *
MEAN OIL DROP DIAMETER (um)	121.0811
CRITICAL OIL DROP DIAM (um)	101.6762
DISPERSING WIND SPEED (m/s)	4.5 *
RESURFACING WIND SPEED (m/s)	4.5 *
DISPERSING DEPTH (m)	2 *
RISING VELOCITY (mm/s)	0
SUSPENSION VELOCITY (mm/s)	0
DISPERSION MEAS TIME (min)	185 *
FRACTION RESURFACED	.4318244
TRANSITION THICKNESS (um)	281.9047

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY PERFORMANCE ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	3.520286	.1802281	3.700514
PERCENT DISPERSED	36.20546	65.0831	37.00514
REMAINING OIL VOLUMES (m3)	6.202794	9.669186E-02	6.299486
REMAINING OIL THICKNESS (mm)	1.375953	3.491689E-03	.1956362
WATER CONCN TIME ZERO (ppm)	390.4487	3.254155	57.4614
WATER CONCN MEAS TIME (ppm)	221.8435	3.254155	33.85666
OIL REMAINING DISPERSED	2.000141	.1802281	2.180369
PERCENT REMAINING DISPERSED	20.57106	65.0831	21.80369

Figure 5.2
ESSO-UK 1982

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	16.85	3.15	20 *
SLICK AREA (m2)	35000	315000	350000 *
SLICK THICKNESS (mm)	.4814286	.01	5.714286E-02
FRACTIONAL AREAS	.1 *	.9	
DISPERSANT APPLIED (m3)	.2	1.8	2 *
DISPERSANT FRACTIONS APPLIED	.1 *	.9	
OIL TO DISPERSANT RATIO	84.25	1.75	10
NUMBER OF DROPS (MILLIONS)	5971.339	53742.04	59713.38
DROPS PER SQUARE CM	17.06097	17.06097	17.06097
DROP SPACING (mm)	2.421019	2.421019	2.421019
DISPERSANT DOSAGE (L/ha)	57.14286	57.14286	57.14286
DISPERSANT DROP DIAM (um)	400 *		
POTENTIAL DISPERSION RATIO	14.28572		
POTNTL DISPSN RATIO AT 7 m/s	50 *		
ACCESSIBLE OIL RATIO	5		
OIL DENSITY (kg/m3)	890 *		
TEMPERATURE (deg C)	11 *		
MEAN OIL DROP DIAMETER (um)	224		
CRITICAL OIL DROP DIAM (um)	127.401		
DISPERSING WIND SPEED (m/s)	2.5 *		
RESURFACING WIND SPEED (m/s)	2.5 *		
DISPERSING DEPTH (m)	2 *		
RISING VELOCITY (mm/s)	0		
SUSPENSION VELOCITY (mm/s)	0		
DISPERSION MEAS TIME (min)	60 *		
FRACTION RESURFACED	.5662304		
TRANSITION THICKNESS (um)	152.381		

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY PERFORMANCE ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	2.857144	1.306459	4.163602
PERCENT DISPERSED	16.95634	41.47489	20.81801
REMAINING OIL VOLUMES (m3)	13.99286	1.843541	15.8364
REMAINING OIL THICKNESS (mm)	.3997959	5.852511E-03	4.524685E-02
WATER CONCN TIME ZERO (ppm)	40.81634	2.073744	5.948004
WATER CONCN MEAS TIME (ppm)	17.70489	2.073744	3.636859
OIL REMAINING DISPERSED	1.239342	1.306459	2.545801
PERCENT REMAINING DISPERSED	7.355146	41.47489	12.72901

Figure 5.3:
HALIFAX 1983 9527

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	2.26	.24	2.5 *
SLICK AREA (m2)	6000	24000	30000 *
SLICK THICKNESS (mm)	.3766667	.01	8.333334E-02
FRACTIONAL AREAS	.2 *	.8	
DISPERSANT APPLIED (m3)	9.269999E-03	.08343	.0927 *
DISPERSANT FRACTIONS APPLIED	.1 *	.9	
OIL TO DISPERSANT RATIO	243.7972	2.876663	26.96872
NUMBER OF DROPS (MILLIONS)	51.6425	464.7825	516.4251
DROPS PER SQUARE CM	.8607084	1.936594	1.721417
DROP SPACING (mm)	10.77884	7.185893	7.621791
DISPERSANT DOSAGE (L/ha)	15.45	34.7625	30.9

DISPERSANT DROP DIAM (um)	700 *
POTENTIAL DISPERSION RATIO	47.77778
POTNTL DISPSN RATIO AT 7 m/s	50 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	820 *
TEMPERATURE (deg C)	18 *
MEAN OIL DROP DIAMETER (um)	66.97675
CRITICAL OIL DROP DIAM (um)	190.1918
DISPERSING WIND SPEED (m/s)	7 *
RESURFACING WIND SPEED (m/s)	7 *
DISPERSING DEPTH (m)	2 *
RISING VELOCITY (mm/s)	0
SUSPENSION VELOCITY (mm/s)	0
DISPERSION MEAS TIME (min)	30 *
FRACTION RESURFACED	5.844501E-02
TRANSITION THICKNESS (um)	891.8518

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY ACCESS ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	.1795235	4.077971E-02	.2203032
PERCENT DISPERSED	7.943517	16.99155	8.812127
REMAINING OIL VOLUMES (m3)	2.080477	.1992203	2.279697
REMAINING OIL THICKNESS (mm)	.3467461	8.300846E-03	.0759899
WATER CONCN TIME ZERO (ppm)	14.96029	.8495773	3.67172
WATER CONCN MEAS TIME (ppm)	14.08594	.8495773	3.496849
OIL REMAINING DISPERSED	.1690312	4.077971E-02	.2098109
PERCENT REMAINING DISPERSED	7.479258	16.99155	8.392437

Figure 5.4:
HALIFAX 1983 9550

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	2.26	.24	2.5 *
SLICK AREA (m2)	6000	24000	30000 *
SLICK THICKNESS (mm)	.3766667	.01	8.333334E-02
FRACTIONAL AREAS	.2 *	.8	
DISPERSANT APPLIED (m3)	.0626	.2504	.313 *
DISPERSANT FRACTIONS APPLIED	.2 *	.8	
OIL TO DISPERSANT RATIO	36.10224	.9584664	7.987221
NUMBER OF DROPS (MILLIONS)	348.7401	1394.96	1743.701
DROPS PER SQUARE CM	5.812335	5.812335	5.812335
DROP SPACING (mm)	4.147866	4.147866	4.147866
DISPERSANT DOSAGE (L/ha)	104.3333	104.3333	104.3333
DISPERSANT DROP DIAM (um)	700 *		
POTENTIAL DISPERSION RATIO	8.190476		
POTNTL DISPSN RATIO AT 7 m/s	10 *		
ACCESSIBLE OIL RATIO	5		
OIL DENSITY (kg/m3)	820 *		
TEMPERATURE (deg C)	18 *		
MEAN OIL DROP DIAMETER (um)	390.6977		
CRITICAL OIL DROP DIAM (um)	383.6693		
DISPERSING WIND SPEED (m/s)	6 *		
RESURFACING WIND SPEED (m/s)	6 *		
DISPERSING DEPTH (m)	2 *		
RISING VELOCITY (mm/s)	0		
SUSPENSION VELOCITY (mm/s)	0		
DISPERSION MEAS TIME (min)	3 *		
FRACTION RESURFACED	.3745573		
TRANSITION THICKNESS (um)	152.8889		

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY PERFORMANCE ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	.5127238	.1027629	.6154867
PERCENT DISPERSED	22.68689	42.81786	24.61947
REMAINING OIL VOLUMES (m3)	1.747276	.1372371	1.884513
REMAINING OIL THICKNESS (mm)	.2912127	5.718214E-03	6.281711E-02
WATER CONCN TIME ZERO (ppm)	42.72698	2.140893	10.25811
WATER CONCN MEAS TIME (ppm)	26.72328	2.140893	7.057371
OIL REMAINING DISPERSED	.3206794	.1027629	.4234423
PERCENT REMAINING DISPERSED	14.18935	42.81786	16.93769

Figure 5.5:

HALIFAX 1983 BP MA700

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	2.26	.24	2.5 *
SLICK AREA (m2)	6000	24000	30000 *
SLICK THICKNESS (mm)	.3766667	.01	8.333334E-02
FRACTIONAL AREAS	.2 *	.8	
DISPERSANT APPLIED (m3)	.0556	.2224	.278 *
DISPERSANT FRACTIONS APPLIED	.2 *	.8	
OIL TO DISPERSANT RATIO	40.64749	1.079137	8.992806
NUMBER OF DROPS (MILLIONS)	309.7436	1238.975	1548.718
DROPS PER SQUARE CM	5.162394	5.162394	5.162394
DROP SPACING (mm)	4.401234	4.401234	4.401234
DISPERSANT DOSAGE (L/ha)	92.66666	92.66666	92.66666
DISPERSANT DROP DIAM (um)	700 *		
POTENTIAL DISPERSION RATIO	106.4762		
POTNTL DISPSN RATIO AT 7 m/s	60 *		
ACCESSIBLE OIL RATIO	5		
OIL DENSITY (kg/m3)	820 *		
TEMPERATURE (deg C)	18 *		
MEAN OIL DROP DIAMETER (um)	30.05367		
CRITICAL OIL DROP DIAM (um)	249.7293		
DISPERSING WIND SPEED (m/s)	13 *		
RESURFACING WIND SPEED (m/s)	13 *		
DISPERSING DEPTH (m)	2 *		
RISING VELOCITY (mm/s)	0		
SUSPENSION VELOCITY (mm/s)	0		
DISPERSION MEAS TIME (min)	30 *		
FRACTION RESURFACED	2.461803E-04		
TRANSITION THICKNESS (um)	1987.556		

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY ACCESS ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	.8843365	9.391182E-02	.9782483
PERCENT DISPERSED	39.12993	39.12993	39.12993
REMAINING OIL VOLUMES (m3)	1.375664	.1460882	1.521752
REMAINING OIL THICKNESS (mm)	.2292773	6.087007E-03	5.072506E-02
WATER CONCN TIME ZERO (ppm)	73.69471	1.956497	16.30414
WATER CONCN MEAS TIME (ppm)	73.67657	1.956497	16.30051
OIL REMAINING DISPERSED	.8841188	9.391182E-02	.9780306
PERCENT REMAINING DISPERSED	39.1203	39.12993	39.12122

Figure 5.6:
NEW JERSEY 1978 LA ROSA

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	1.55	.12	1.67 *
SLICK AREA (m2)	8000	12000	20000 *
SLICK THICKNESS (mm)	.19375	.01	.0835
FRACTIONAL AREAS	.4 *	.6	
DISPERSANT APPLIED (m3)	.105	.045	.15 *
DISPERSANT FRACTIONS APPLIED	.7 *	.3	
OIL TO DISPERSANT RATIO	14.7619	2.666667	11.13333
NUMBER OF DROPS (MILLIONS)	3134.953	1343.551	4478.504
DROPS PER SQUARE CM	39.18691	11.19626	22.39252
DROP SPACING (mm)	1.597458	2.988571	2.113239
DISPERSANT DOSAGE (L/ha)	131.25	37.5	75

DISPERSANT DROP DIAM (um)	400 *
POTENTIAL DISPERSION RATIO	18.57143
POTNTL DISPSN RATIO AT 7 m/s	30 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	910 *
TEMPERATURE (deg C)	14 *
MEAN OIL DROP DIAMETER (um)	172.3077
CRITICAL OIL DROP DIAM (um)	221.9893
DISPERSING WIND SPEED (m/s)	5 *
RESURFACING WIND SPEED (m/s)	5 *
DISPERSING DEPTH (m)	2 *
RISING VELOCITY (mm/s)	0
SUSPENSION VELOCITY (mm/s)	0
DISPERSION MEAS TIME (min)	30 *
FRACTION RESURFACED	.2757307
TRANSITION THICKNESS (um)	198.0952

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY ACCESS ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	1.097159	3.556945E-02	1.132728
PERCENT DISPERSED	70.78445	29.64121	67.82805
REMAINING OIL VOLUMES (m3)	.4528411	8.443054E-02	.5372716
REMAINING OIL THICKNESS (mm)	5.660514E-02	7.035879E-03	2.686358E-02
WATER CONCN TIME ZERO (ppm)	68.57243	1.482061	28.31821
WATER CONCN MEAS TIME (ppm)	49.66492	1.482061	20.7552
OIL REMAINING DISPERSED	.7946386	3.556945E-02	.8302081
PERCENT REMAINING DISPERSED	51.26702	29.64121	49.71306

Figure: 5.7:
NEW JERSEY 1978 MURBAN

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	1.55	.12	1.67 *
SLICK AREA (m2)	8000	12000	20000 *
SLICK THICKNESS (mm)	.19375	.01	.0835
FRACTIONAL AREAS	.4 *	.6	
DISPERSANT APPLIED (m3)	.105	.045	.15 *
DISPERSANT FRACTIONS APPLIED	.7 *	.3	
OIL TO DISPERSANT RATIO	14.7619	2.666667	11.13333
NUMBER OF DROPS (MILLIONS)	3134.953	1343.551	4478.504
DROPS PER SQUARE CM	39.18691	11.19626	22.39252
DROP SPACING (mm)	1.597458	2.988571	2.113239
DISPERSANT DOSAGE (L/ha)	131.25	37.5	75

DISPERSANT DROP DIAM (um)	400 *
POTENTIAL DISPERSION RATIO	30.95238
POTNTL DISPSN RATIO AT 7 m/s	50 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	830 *
TEMPERATURE (deg C)	14 *
MEAN OIL DROP DIAMETER (um)	103.3846
CRITICAL OIL DROP DIAM (um)	170.1703
DISPERSING WIND SPEED (m/s)	5 *
RESURFACING WIND SPEED (m/s)	5 *
DISPERSING DEPTH (m)	2 *
RISING VELOCITY (mm/s)	0
SUSPENSION VELOCITY (mm/s)	0
DISPERSION MEAS TIME (min)	30 *
FRACTION RESURFACED	.1928212
TRANSITION THICKNESS (um)	330.1587

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY ACCESS ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	1.097159	3.556945E-02	1.132728
PERCENT DISPERSED	70.78445	29.64121	67.82805
REMAINING OIL VOLUMES (m3)	.4528411	8.443054E-02	.5372716
REMAINING OIL THICKNESS (mm)	5.660514E-02	7.035879E-03	2.686358E-02
WATER CONCN TIME ZERO (ppm)	68.57243	1.482061	28.31821
WATER CONCN MEAS TIME (ppm)	55.35022	1.482061	23.02932
OIL REMAINING DISPERSED	.8856035	3.556945E-02	.9211729
PERCENT REMAINING DISPERSED	57.13571	29.64121	55.16006

Figure 5.8:
SOUTH CALIFORNIA 1979

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	3.0225	.1575	3.18 *
SLICK AREA (m2)	6750	15750	22500 *
SLICK THICKNESS (mm)	.4477778	.01	.1413333
FRACTIONAL AREAS	.3 *	.7	
DISPERSANT APPLIED (m3)	.06	.06	.12 *
DISPERSANT FRACTIONS APPLIED	.5 *	.5	
OIL TO DISPERSANT RATIO	50.375	2.625	26.5
NUMBER OF DROPS (MILLIONS)	1791.402	1791.402	3582.803
DROPS PER SQUARE CM	26.53928	11.37398	15.92357
DROP SPACING (mm)	1.941134	2.965131	2.505993
DISPERSANT DOSAGE (L/ha)	88.88889	38.09524	53.33333

DISPERSANT DROP DIAM (um)	400 *
POTENTIAL DISPERSION RATIO	31.74604
POTNTL DISPSN RATIO AT 7 m/s	50 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	890 *
TEMPERATURE (deg C)	15 *
MEAN OIL DROP DIAMETER (um)	100.8
CRITICAL OIL DROP DIAM (um)	204.7539
DISPERSING WIND SPEED (m/s)	5 *
RESURFACING WIND SPEED (m/s)	5 *
DISPERSING DEPTH (m)	2 *
RISING VELOCITY (mm/s)	0
SUSPENSION VELOCITY (mm/s)	0
DISPERSION MEAS TIME (min)	30 *
FRACTION RESURFACED	.1311664
TRANSITION THICKNESS (um)	338.6244

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY PERFORMANCE AND ACCESS

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	1.651296	4.730158E-02	1.698598
PERCENT DISPERSED	54.63346	30.03275	53.41502
REMAINING OIL VOLUMES (m3)	1.371204	.1101984	1.481402
REMAINING OIL THICKNESS (mm)	.2031413	6.996726E-03	.0658401
WATER CONCN TIME ZERO (ppm)	122.3182	1.501637	37.74662
WATER CONCN MEAS TIME (ppm)	106.2742	1.501637	32.9334
OIL REMAINING DISPERSED	1.434702	4.730158E-02	1.482003
PERCENT REMAINING DISPERSED	47.46738	30.03275	46.60387

Figure 5.9:
DUTCH 1983 NO 4

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	1.51	.49	2 *
SLICK AREA (m2)	21000	49000	70000 *
SLICK THICKNESS (mm)	7.190476E-02	.01	2.857143E-02
FRACTIONAL AREAS	.3 *	.7	
DISPERSANT APPLIED (m3)	.03	.07	.1 *
DISPERSANT FRACTIONS APPLIED	.3 *	.7	
OIL TO DISPERSANT RATIO	50.33333	7	20
NUMBER OF DROPS (MILLIONS)	895.7008	2089.968	2985.669
DROPS PER SQUARE CM	4.265242	4.265242	4.265242
DROP SPACING (mm)	4.842038	4.842038	4.842038
DISPERSANT DOSAGE (L/ha)	14.28571	14.28571	14.28571

DISPERSANT DROP DIAM (um)	400 *
POTENTIAL DISPERSION RATIO	2.730159
POTNTL DISPSN RATIO AT 7 m/s	10 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	852 *
TEMPERATURE (deg C)	18 *
MEAN OIL DROP DIAMETER (um)	1172.093
CRITICAL OIL DROP DIAM (um)	104.4518
DISPERSING WIND SPEED (m/s)	2 *
RESURFACING WIND SPEED (m/s)	2 *
DISPERSING DEPTH (m)	2 *
MEAN RISING VELOCITY (mm/s)	128.7802
SUSPENSION VELOCITY (mm/s)	.8599999
DISPERSION MEAS TIME (min)	60 *
FRACTION RESURFACED	.9147399
TRANSITION THICKNESS (um)	29.12169

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY PERFORMANCE ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	8.190477E-02	6.142026E-02	.143325
PERCENT DISPERSED	5.424157	12.53475	7.166252
REMAINING OIL VOLUMES (m3)	1.428095	.4285797	1.856675
REMAINING OIL THICKNESS (mm)	6.800453E-02	8.746525E-03	2.652393E-02
WATER CONCN TIME ZERO (ppm)	1.950113	.6267374	1.02375
WATER CONCN MEAS TIME (ppm)	.166267	.6267374	.4885963
OIL REMAINING DISPERSED	6.983213E-03	6.142026E-02	6.840348E-02
PERCENT REMAINING DISPERSED	.4624645	12.53475	3.420174

Figure 5.10:
DUTCH 1983 NO 6

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	1.65	.35	2 *
SLICK AREA (m2)	15000	35000	50000 *
SLICK THICKNESS (mm)	.11	.01	.04
FRACTIONAL AREAS	.3 *	.7	
DISPERSANT APPLIED (m3)	8.999999E-02	1.000001E-02	.1 *
DISPERSANT FRACTIONS APPLIED	.9 *	.1	
OIL TO DISPERSANT RATIO	18.33333	34.99998	20
NUMBER OF DROPS (MILLIONS)	2687.102	298.567	2985.669
DROPS PER SQUARE CM	17.91401	.8530486	5.971339
DROP SPACING (mm)	2.362673	10.82713	4.092269
DISPERSANT DOSAGE (L/ha)	60	2.857144	20

DISPERSANT DROP DIAM (um)	400 *
POTENTIAL DISPERSION RATIO	109.2064
POTNTL DISPSN RATIO AT 7 m/s	100 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	852 *
TEMPERATURE (deg C)	18 *
MEAN OIL DROP DIAMETER (um)	29.30233
CRITICAL OIL DROP DIAM (um)	180.5734
DISPERSING WIND SPEED (m/s)	8 *
RESURFACING WIND SPEED (m/s)	8 *
DISPERSING DEPTH (m)	2 *
RISING VELOCITY (mm/s)	0
SUSPENSION VELOCITY (mm/s)	0
DISPERSION MEAS TIME (min)	60 *
FRACTION RESURFACED	2.10714E-03
TRANSITION THICKNESS (um)	1164.868

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY ACCESS ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	.7098583	9.250551E-03	.7191088
PERCENT DISPERSED	43.02172	2.643015	35.95544
REMAINING OIL VOLUMES (m3)	.9401417	.3407495	1.280891
REMAINING OIL THICKNESS (mm)	6.267611E-02	9.735699E-03	2.561782E-02
WATER CONCN TIME ZERO (ppm)	23.66194	.1321507	7.191088
WATER CONCN MEAS TIME (ppm)	23.61208	.1321507	7.176131
OIL REMAINING DISPERSED	.7083625	9.250551E-03	.7176131
PERCENT REMAINING DISPERSED	42.93106	2.643015	35.88065

Figure 5.11:
DUTCH 1983 NO 9

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	1.51	.49	2 *
SLICK AREA (m2)	21000	49000	70000 *
SLICK THICKNESS (mm)	7.190476E-02	.01	2.857143E-02
FRACTIONAL AREAS	.3 *	.7	
DISPERSANT APPLIED (m3)	.03	.07	.1 *
DISPERSANT FRACTIONS APPLIED	.3 *	.7	
OIL TO DISPERSANT RATIO	50.33333	7	20
NUMBER OF DROPS (MILLIONS)	895.7008	2089.968	2985.669
DROPS PER SQUARE CM.	4.265242	4.265242	4.265242
DROP SPACING (mm)	4.842038	4.842038	4.842038
DISPERSANT DOSAGE (L/ha)	14.28571	14.28571	14.28571

DISPERSANT DROP DIAM (um)	400 *
POTENTIAL DISPERSION RATIO	8.888889
POTNTL DISPSN RATIO AT 7 m/s	10 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	852 *
TEMPERATURE (deg C)	15 *
MEAN OIL DROP DIAMETER (um)	360
CRITICAL OIL DROP DIAM (um)	170.1204
DISPERSING WIND SPEED (m/s)	7 *
RESURFACING WIND SPEED (m/s)	7 *
DISPERSING DEPTH (m)	2 *
RISING VELOCITY (mm/s)	0
SUSPENSION VELOCITY (mm/s)	0
DISPERSION MEAS TIME (min)	60 *
FRACTION RESURFACED	.6234065
TRANSITION THICKNESS (um)	94.81481

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY ACCESS ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	.1892748	6.142026E-02	.2506951
PERCENT DISPERSED	12.53475	12.53475	12.53475
REMAINING OIL VOLUMES (m3)	1.320725	.4285797	1.749305
REMAINING OIL THICKNESS (mm)	6.289168E-02	8.746525E-03	2.499007E-02
WATER CONCN TIME ZERO (ppm)	4.506542	.6267374	1.790679
WATER CONCN MEAS TIME (ppm)	1.697135	.6267374	.9478567
OIL REMAINING DISPERSED	7.127968E-02	6.142026E-02	.1328999
PERCENT REMAINING DISPERSED	4.720508	12.53475	6.634997

Figure 5.12:
ROTATING FLASK TEST

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	4.9999E-06	9.999991E-11	.000005 *
SLICK AREA (m2)	9.900001E-04	9.999991E-06	.001 *
SLICK THICKNESS (mm)	5.050404	.01	5
FRACTIONAL AREAS	.99 *	9.999991E-03	
DISPERSANT APPLIED (m3)	7.425001E-08	7.499992E-10	7.5E-08 *
DISPERSANT FRACTIONS APPLIED	.99 *	9.999991E-03	
OIL TO DISPERSANT RATIO	67.33871	.1333334	66.66666
NUMBER OF DROPS (MILLIONS)	1.41879E-04	1.43312E-06	1.433121E-04
DROPS PER SQUARE CM	14.33121	14.33121	14.33121
DROP SPACING (mm)	2.641548	2.641548	2.641548
DISPERSANT DOSAGE (L/ha)	750	749.9999	750

DISPERSANT DROP DIAM (um)	1000 *
POTENTIAL DISPERSION RATIO	28.57143
POTNTL DISPSN RATIO AT 7 m/s	50 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	800 *
TEMPERATURE (deg C)	20 *
MEAN OIL DROP DIAMETER (um)	112
CRITICAL OIL DROP DIAM (um)	82.62036
DISPERSING WIND SPEED (m/s)	4 *
RESURFACING WIND SPEED (m/s)	0 *
DISPERSING DEPTH (m)	.1 *
RISING VELOCITY (mm/s)	0
SUSPENSION VELOCITY (mm/s)	0
DISPERSION MEAS TIME (min)	2 *
FRACTION RESURFACED	.4782213
TRANSITION THICKNESS (um)	761.9047

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY PERFORMANCE ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	2.121429E-06	9.399444E-11	2.121522E-06
PERCENT DISPERSED	42.42942	93.99453	42.43045
REMAINING OIL VOLUMES (m3)	2.878472E-06	6.005465E-12	2.878478E-06
REMAINING OIL THICKNESS (mm)	2.907547	6.00547E-04	2.878477
WATER CONCN TIME ZERO (ppm)	21428.57	93.99452	21215.22
WATER CONCN MEAS TIME (ppm)	11180.97	93.99452	11070.1
OIL REMAINING DISPERSED	1.106916E-06	9.399444E-11	1.10701E-06
PERCENT REMAINING DISPERSED	22.13877	93.99453	22.14021

Figure 5.13:
MNS TEST

NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	9.999619E-06	3.799997E-10	.00001 *
SLICK AREA (m2)	.003762	3.799997E-05	.0038 *
SLICK THICKNESS (mm)	2.658059	.01	2.631579
FRACTIONAL AREAS	.99 *	9.999991E-03	
DISPERSANT APPLIED (m3)	1.485E-07	1.499998E-09	1.5E-07 *
DISPERSANT FRACTIONS APPLIED	.99 *	9.999991E-03	
OIL TO DISPERSANT RATIO	67.3375	.2533334	66.66666
NUMBER OF DROPS (MILLIONS)	2.83758E-04	2.86624E-06	2.866243E-04
DROPS PER SQUARE CM	7.542743	7.542743	7.542743
DROP SPACING (mm)	3.641123	3.641123	3.641123
DISPERSANT DOSAGE (L/ha)	394.7369	394.7368	394.7368

DISPERSANT DROP DIAM (um)	1000 *
POTENTIAL DISPERSION RATIO	35.71429
POTNTL DISPSN RATIO AT 7 m/s	50 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	800 *
TEMPERATURE (deg C)	20 *
MEAN OIL DROP DIAMETER (um)	89.6
CRITICAL OIL DROP DIAM (um)	187.7698
DISPERSING WIND SPEED (m/s)	5 *
RESURFACING WIND SPEED (m/s)	5 *
DISPERSING DEPTH (m)	.085 *
RISING VELOCITY (mm/s)	0
SUSPENSION VELOCITY (mm/s)	0
DISPERSION MEAS TIME (min)	10 *
FRACTION RESURFACED	.1229909
TRANSITION THICKNESS (um)	952.3809

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY PERFORMANCE ONLY

	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	5.303572E-06	2.935202E-10	5.303865E-06
PERCENT DISPERSED	53.03774	77.24222	53.03866
REMAINING OIL VOLUMES (m3)	4.696048E-06	8.647951E-11	4.696135E-06
REMAINING OIL THICKNESS (mm)	1.248285	2.275779E-03	1.235825
WATER CONCN TIME ZERO (ppm)	16585.58	90.87319	16420.64
WATER CONCN MEAS TIME (ppm)	14545.71	90.87319	14401.16
OIL REMAINING DISPERSED	4.651281E-06	2.935202E-10	4.651575E-06
PERCENT REMAINING DISPERSED	46.51458	77.24222	46.51575

$$DP = 3200/X \ (\mu m)$$

In most cases by adjusting the fractional areas and dosages within reasonable limits it is possible to reproduce the observed effectiveness with satisfactory accuracy. The main exceptions are the Halifax trials which seemed to give unusually low effectivenesses. This could be due to dispersant drop diameter. Use of a 700 um drop diameter gave better results than the usual 400 um.

There is a trend for the model to overpredict effectiveness for the "unsuccessful" trials such as the Esso-UK and Dutch tests. The reason for this is not clear.

There is some apparent internal inconsistency between some experimental results. For example the New Jersey and California results are much better than the Halifax results but conditions were quite similar. The model can serve a useful purpose in highlighting such inconsistencies.

In general, the model is regarded as being a significant step towards quantifying the processes of oceanic and laboratory dispersion and linking these regimes. It suggests that the principal reason for frequent unsuccessful oceanic tests is under and over dosing. This is particularly likely on small spills in which there is a higher proportion of sheen and the "target" of the thick slick is smaller and more difficult to hit. It can be used in a predictive exploratory mode to examine the implications of various application strategies.

Finally, it is emphasised that this model is only a step towards the ultimate goal of a reliable, validated model. The expressions used are the current best estimates and are subject to change in the light of new information.

The model should thus be regarded as a dynamic tool for use in improving the science and technology of dispersion, and it is hoped that it will be improved by future studies.

6. CONCLUSIONS.

1) It is believed that the principal reason for occasional poor effectiveness results in experimental spills is the underdosing of thick oil slicks and the overdosing of sheen.

2) This dosing problem will tend to be most severe for small oil spills in which the thick oil target is small. It is thus likely that in a real spill incident with large oil volumes effectiveness will be greater.

3) In future experimental spills it is essential that the DOR values be estimated separately for thick and sheen slicks. An average DOR value is not useful. Complementary laboratory tests should be conducted.

4) There is an incentive to devise better methods of measuring oil slick thickness before and after dispersion for effectiveness assessment purposes, and as a guide to those applying dispersants. A remote sensing system is preferred.

5) Measurement of effectiveness by taking water samples alone is unlikely to give reliable data. The aim should be to measure the amount remaining on the surface.

6) It is apparently necessary to test each oil with each candidate dispersant at the relevant temperature(s) and salinity.

7) It is suggested that in any test program for dispersant selection both the MNS and RF tests be used since they give different information. From such test results it should be possible to estimate a dispersant performance parameter X which can be used to estimate volumes of dispersant stockpiles necessary to treat a given volume of oil.

8) Dispersion at low temperatures is feasible but may require somewhat more dispersant. It is essential, however, to test each oil over the entire temperature range to detect any unusual effect of viscosity or wax precipitation.

9) The oil dispersant mixing process varies widely between oils and should be studied further with a view to devising a suitable test protocol.

10) The effect of herding should be studied as a function of slick properties, and thickness, and dispersant drop diameter.

11) The effect of dispersant drop diameter on dispersion should be studied, since it is postulated here to have a profound effect.

12) A mathematical model of the dispersion process has been assembled and tested against available experimental results. It is inherently capable of linking laboratory and oceanic observations. The model should be tested further and modified where necessary.

Finally, these results suggest that chemical dispersion can play a useful role as an oil spill countermeasure. Further demonstrations of its effectiveness are desirable, but the demonstrations must be designed carefully to avoid further "poor" results. The aim should be to apply dispersant at dosages of 1/20 to 1/40 to thick oils slicks under sufficiently turbulent conditions using products which are proved to be suitable for the oil in question under the prevailing conditions. To do otherwise is to invite poor results which can lead to undue pessimism on the part of approving agencies which could retard or prevent a full and fair assessment of chemical dispersion as an oil spill countermeasure.

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Appendix 1

Computer Program:

```
10 CLS
20 KEY OFF
30 INPUT "SPILL IDENTIFICATION"; SPILL$
40 INPUT "What is total oil volume (m3)(eg 20)";VO
50 INPUT "What is the total spill area (m2) (eg 100000)";AO
60 INPUT "What fraction of the total area is thick (eg 0.2)";FAT
70 INPUT "What volume of dispersant is applied (m3)(eg 1)";VDO
90 PRINT "What fraction of the dispersant was applied to the thick slick?";
100 PRINT "    Note that it has a fraction of the total area of ";FAT
110 PRINT "    If application was even over all the slick area this would be ";
120 PRINT "    the fraction applied to the thick slick (eg 0.3)";
130 INPUT FDT
140 INPUT "What is the average dispersant drop diameter (um) (eg 400)";ZOU
150 INPUT "What is the dispersant performance ratio at 7 m/s & 20 deg C (eg 40)";XB
160 INPUT "What is the oil density (kg/m3)(eg 800)";DEN
170 INPUT "What is the temperature (deg C) (eg 20)";CEL
180 INPUT "What is the actual or equivalent dispersing wind speed (m/s)(eg 5)";UWD
190 INPUT "What is the actual or equivalent resurfacing wind speed (m/s)(eg 5)";UWR
200 INPUT "What is the short term dispersion depth (m)(eg 2)";Y
210 INPUT "What is the measuring time (min)(eg 10)";HM1
220 X=XB*UWD/7*(25+CEL)/45
225 FAS=1-FAT
230 TSU=10
240 Q=5
250 AS=FAS*AO
260 AT=AO-AS
270 TS=TSU/1000000!
280 VS=AS*TS
290 VT=VO-VS:TSM=TS*1000
300 TT=VT/AT:TTM=TT*1000
310 RO=VO/VDO:TOM=1000*VO/AO
320 VDT=VDO*FDT
330 VDS=VDO-VDT
340 RT=VT/VDT
350 RS=VS/VDS
360 GT=1E+07*VDT/AT
370 GS=1E+07*VDS/AS
380 GO=1E+07*VDO/AO
390 ZOU=80*40/X
400 ZD=ZOU/1000000!
410 ZO=ZOU/1000000!
420 NDO=VDO/(3.14*ZD^3/6)
430 FDS=1-FDT
440 NDT=NDO*FDT
450 NDS=NDO*FDS
460 NDOM=NDO/1000000!
470 NDSM=NDS/1000000!
480 NDTM=NDT/1000000!
490 MDO=NDO/AO/10000
500 MDT=NDT/AT/10000
510 MDS=NDS/AS/10000
520 QDO=10/SQR(MDO)
530 QDT=10/SQR(MDT)
```

```
540 QDS=10/SQR(MDS)
550 TB=X*ZD/(1.5*Q*Q)
560 TBU=TB*1000000!
570 VBS=(VS-TB*AS)/X
580 VBT=(VT-TB*AT)/X
590 REM CALCULATE SHEEN DISPERSION
600 IF TB>TS THEN GOTO 610 ELSE GOTO 640
610 SHEEN$="SHEEN DISPERSION IS LIMITED BY ACCESS ONLY"
620 VDPS=0:VDAS=VDS
630 GOTO 700
640 IF VBS>VDS THEN GOTO 650 ELSE GOTO 680
650 SHEEN$="SHEEN DISPERSION IS LIMITED BY PERFORMANCE ONLY"
660 VDPS=VDS:VDAS=0
670 GOTO 700
680 SHEEN$=" SHEEN DISPERSION IS LIMITED BY PERFORMANCE AND ACCESS"
690 VDPS=VBS:VDAS=VDS-VDPS
700 VRS=(VS-X*VDPS)*EXP(-1.5*Q*Q*VDAS/(ZD*AS))
710 VES=VS-VRS:PS=100!*VES/VS
720 REM CALCULATE THICK SLICK DISPERSION
730 IF TB>TT THEN GOTO 740 ELSE GOTO 770
740 THICK$="THICK SLICK DISPERSION IS LIMITED BY ACCESS ONLY"
750 VDPT=0:VDAT=VDT
760 GOTO 830
770 IF VBT>VDT THEN GOTO 780 ELSE GOTO 810
780 THICK$="THICK SLICK DISPERSION IS LIMITED BY PERFORMANCE ONLY"
790 VDPT=VDT:VDAT=0
800 GOTO 830
810 THICK$="THICK SLICK DISPERSION IS LIMITED BY PERFORMANCE AND ACCESS"
820 VDPT=VBT:VDAT=VDT-VDPT
830 VRT=(VT-X*VDPT)*EXP(-1.5*Q*Q*VDAT/(ZD*AT))
840 VET=VT-VRT:PT=100!*VET/VT
850 VEO=VET+VES
860 VRO=VO-VEO
870 PO=100*VEO/VO
880 TRT=VRT/AT:TRTM=TRT*1000
890 TRS=VRS/AS:TRSM=TRS*1000
900 TRO=VRO/AO:TROM=TRO*1000
910 UR=ZO*ZO*(1024-DEN)*9.810001/(18*.001)
920 KE=.00043*UWR*UWR:UT=KE/Y
930 URM=UR*1000:UTM=UT*1000
960 H1=HM1*60
970 UC=(Y+SQR(Y*Y+4*H1*Y*UT))/(2*H1)
980 ZC=SQR(UC*18*.001/((1024-DEN)*9.810001))
990 ZCU=ZC*1000000!
1000 FR1=EXP(-ZC/ZO):FE1=1-FR1
1010 CTP=1000000!*VET/(AT*Y):CTP1=CTP*FE1:VET1=VET*FE1:PT1=100*VET1/VT
1020 CSP=1000000!*VES/(AS*Y):CSP1=CSP:VES1=VES:PS1=100*VES1/VS
1030 COP=1000000!*VEO/(AO*Y):VEO1=VET1+VES1:PO1=100*VEO1/VO:COP1=1000000!*VEO1/(AO*Y)
1040 LPRINT "          * SPILL$
1050 LPRINT " "
1060 LPRINT "NOTE THAT INPUT DATA IS DESIGNATED *"
1070 LPRINT " "
1080 LPRINT TAB(30) "THICK" TAB(45) "SHEEN" TAB(60) "TOTAL"
1090 LPRINT
1100 LPRINT "SLICK VOLUME (m3)" TAB(30) VT TAB(45) VS TAB(60) VO "*"
1110 LPRINT "SLICK AREA (m2)" TAB(30) AT TAB(45) AS TAB(60) AO "*"
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```
1120 LPRINT "SLICK THICKNESS (mm)" TAB(30) TTM TAB(45) TSM TAB(60) TOM
1130 LPRINT "FRACTIONAL AREAS" TAB(30) FAT "*" TAB(45) FAS
1140 LPRINT "DISPERSANT APPLIED (m3)" TAB(30) VDT TAB(45) VDS TAB(60) VDO "*"
1150 LPRINT "DISPERSANT FRACTIONS APPLIED" TAB(30) FDT "*" TAB(45) FDS
1160 LPRINT "OIL TO DISPERSANT RATIO" TAB(30) RT TAB(45) RS TAB(60) RO
1170 LPRINT "NUMBER OF DROPS (MILLIONS)" TAB(30) NDTM TAB(45) NDSM TAB(60) NDOM
1180 LPRINT "DROPS PER SQUARE CM" TAB(30) NDT TAB(45) NDS TAB(60) NDO
1190 LPRINT "DROP SPACING (mm)" TAB(30) QDT TAB(45) QDS TAB(60) QDO
1200 LPRINT "DISPERSANT DOSAGE (L/ha)" TAB(30) GT TAB(45) GS TAB(60) GO
1210 LPRINT " "
1220 LPRINT "DISPERSANT DROP DIAM (um)"TAB(30) ZDU "*"
1230 LPRINT "POTENTIAL DISPERSION RATIO" TAB(30) X
1240 LPRINT "POTNTL DISPSN RATIO AT 7 m/s" TAB(30) XB "*"
1250 LPRINT "ACCESSIBLE OIL RATIO" TAB(30) Q
1260 LPRINT "OIL DENSITY (kg/m3)" TAB(30) DEN "*"
1270 LPRINT "TEMPERATURE (deg C)" TAB(30) CEL "*"
1280 LPRINT "MEAN OIL DROP DIAMETER (um)" TAB(30) ZOU
1290 LPRINT "CRITICAL OIL DROP DIAM (um)" TAB(30) ZCU
1300 LPRINT "DISPERSING WIND SPEED (m/s)" TAB(30) UWD "*"
1310 LPRINT "RESURFACING WIND SPEED (m/s)" TAB(30) UWR "*"
1330 LPRINT "DISPERSING DEPTH (m)" TAB(30) Y "*"
1340 LPRINT "MEAN RISING VELOCITY (mm/s)" TAB(30) URM
1350 LPRINT "SUSPENSION VELOCITY (mm/s)" TAB(30) UTM
1360 LPRINT "DISPERSION MEAS TIME (min)" TAB(30) HM1 "*"
1370 LPRINT "FRACTION RESURFACED" TAB(30) FR1
1380 LPRINT "TRANSITION THICKNESS (um)" TAB(30) TBU
1390 LPRINT " "
1400 LPRINT SHEEN$
1410 LPRINT THICK$
1420 LPRINT " "
1430 LPRINT TAB(30) "THICK" TAB(45) "SHEEN" TAB(60) "TOTAL"
1440 LPRINT " "
1450 LPRINT "ACTUAL OIL DISPERSED" TAB(30) VET TAB(45) VES TAB(60) VEO
1460 LPRINT "PERCENT DISPERSED" TAB(30) PT TAB(45) PS TAB(60) PO
1470 LPRINT " "
1480 LPRINT "REMAINING OIL VOLUMES (m3)" TAB(30) VRT TAB(45) VRS TAB(60) VRO
1490 LPRINT "REMAINING OIL THICKNESS (mm)" TAB(30) TRTM TAB(45) TRSM TAB(60) TROM
1500 LPRINT " "
1510 LPRINT "WATER CONCN TIME ZERO (ppm)" TAB(30) CTP TAB(45) CSP TAB(60) COP
1520 LPRINT "WATER CONCN MEAS TIME (ppm)" TAB(30) CTP1 TAB(45) CSP1 TAB(60) COP1
1530 LPRINT " "
1540 LPRINT "OIL REMAINING DISPERSED" TAB(30) VET1 TAB(45) VES1 TAB(60) VEO1
1550 LPRINT "PERCENT REMAINING DISPERSED" TAB(30) PT1 TAB(45) PS1 TAB(60) PO1
1560 LPRINT " "
```

Spill Output:

TEST SPILL

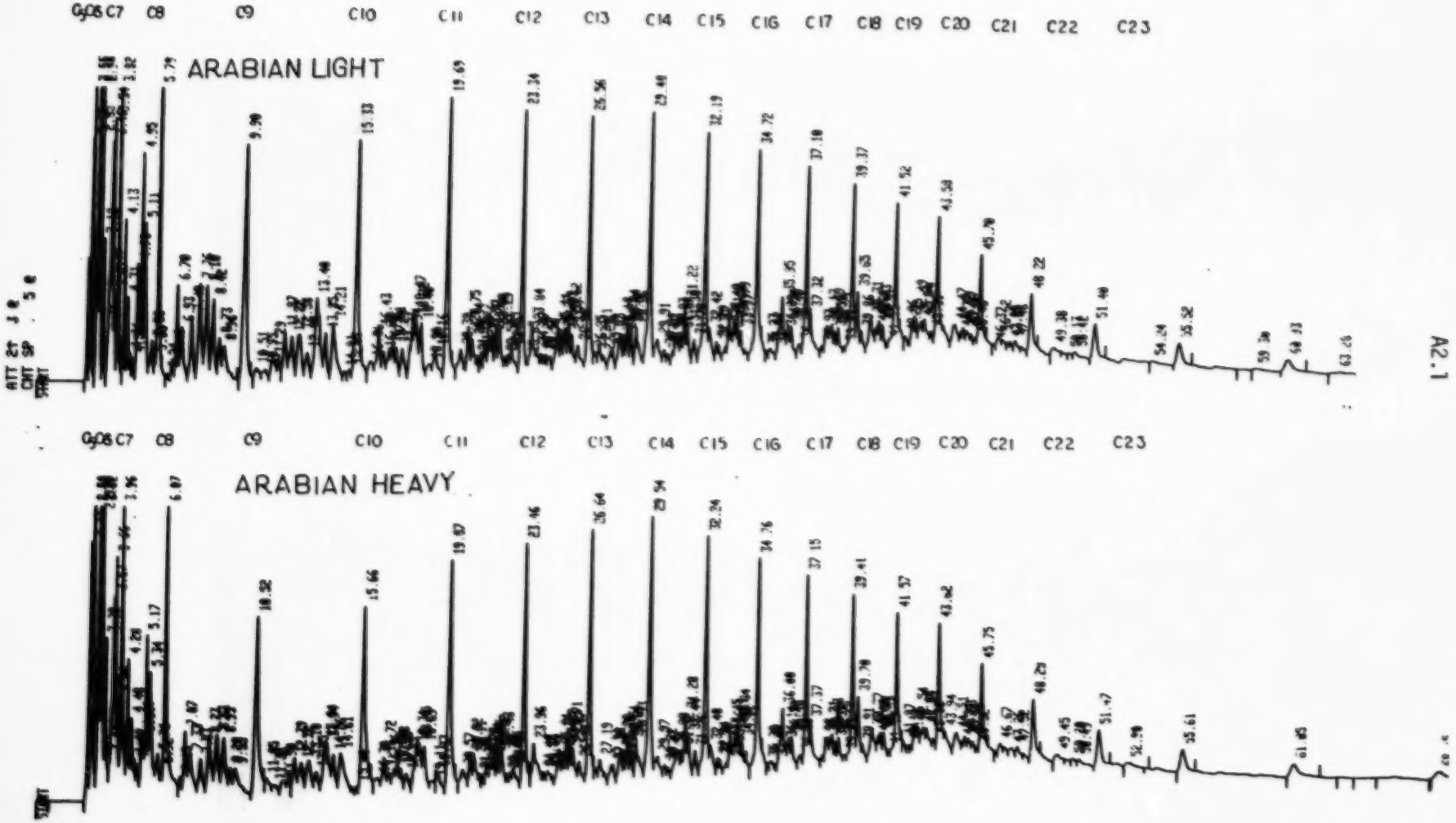
NOTE THAT INPUT DATA IS DESIGNATED *

	THICK	SHEEN	TOTAL
SLICK VOLUME (m3)	19.2	.8	20 *
SLICK AREA (m2)	20000	80000	100000 *
SLICK THICKNESS (mm)	.9600001	.01	.2
FRACTIONAL AREAS	.2 *	.8	
DISPERSANT APPLIED (m3)	.3	.7	1 *
DISPERSANT FRACTIONS APPLIED	.3 *	.7	
OIL TO DISPERSANT RATIO	64	1.142857	20
NUMBER OF DROPS (MILLIONS)	8957.008	20899.68	29856.69
DROPS PER SQUARE CM	44.78504	26.1246	29.85669
DROP SPACING (mm)	1.494285	1.956479	1.830118
DISPERSANT DOSAGE (L/ha)	150	87.5	100

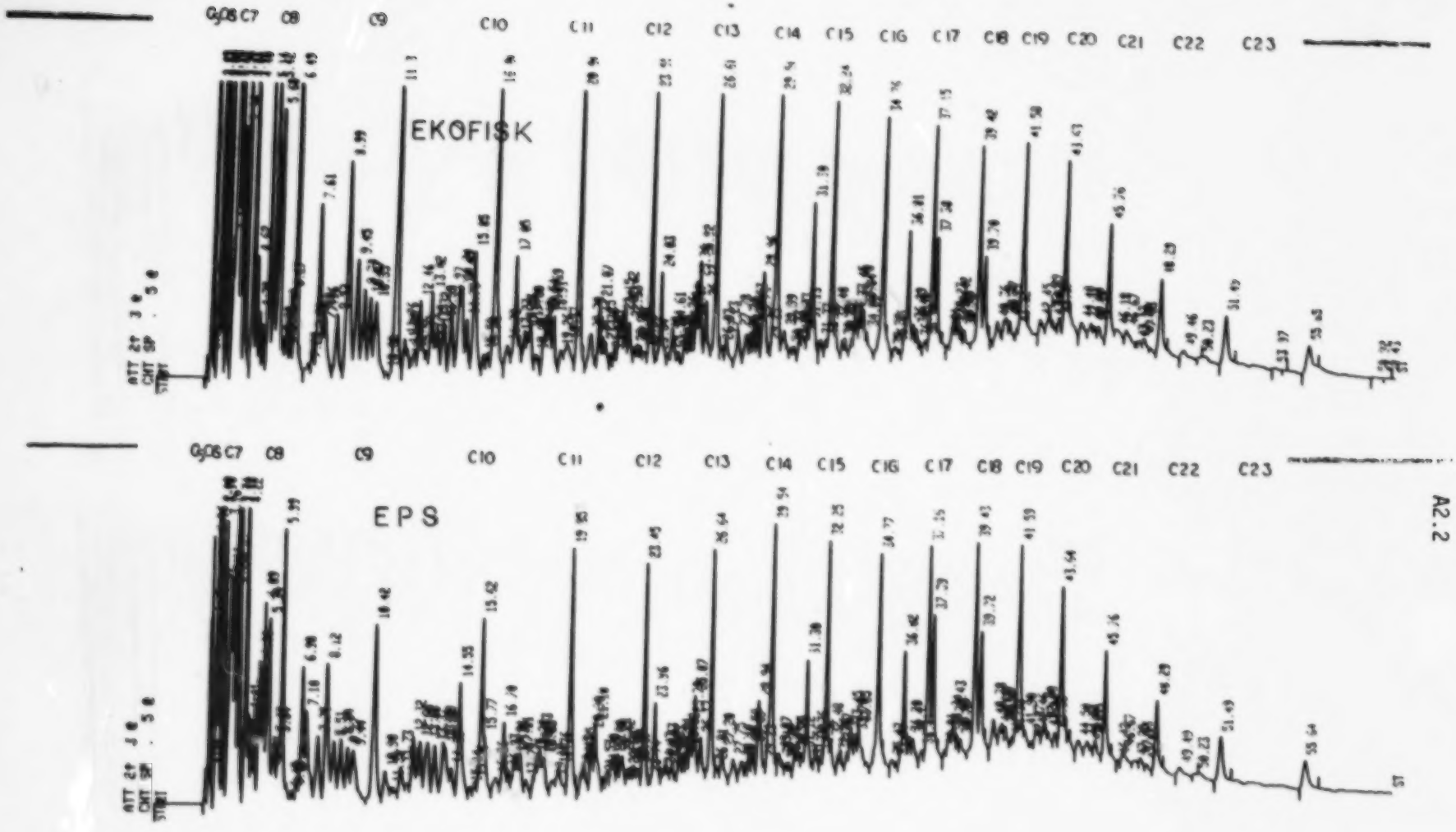
DISPERSANT DROP DIAM (um)	400 *
POTENTIAL DISPERSION RATIO	28.57143
POTNTL DISPSN RATIO AT 7 m/s	40 *
ACCESSIBLE OIL RATIO	5
OIL DENSITY (kg/m3)	800 *
TEMPERATURE (deg C)	20 *
MEAN OIL DROP DIAMETER (um)	112
CRITICAL OIL DROP DIAM (um)	225.6449
DISPERSING WIND SPEED (m/s)	5 *
RESURFACING WIND SPEED (m/s)	5 *
DISPERSING DEPTH (m)	2 *
MEAN RISING VELOCITY (mm/s)	1.531372
SUSPENSION VELOCITY (mm/s)	5.375
DISPERSION MEAS TIME (min)	10 *
FRACTION RESURFACED	.1333622
TRANSITION THICKNESS (um)	304.7619

SHEEN DISPERSION IS LIMITED BY ACCESS ONLY
THICK SLICK DISPERSION IS LIMITED BY PERFORMANCE ONLY

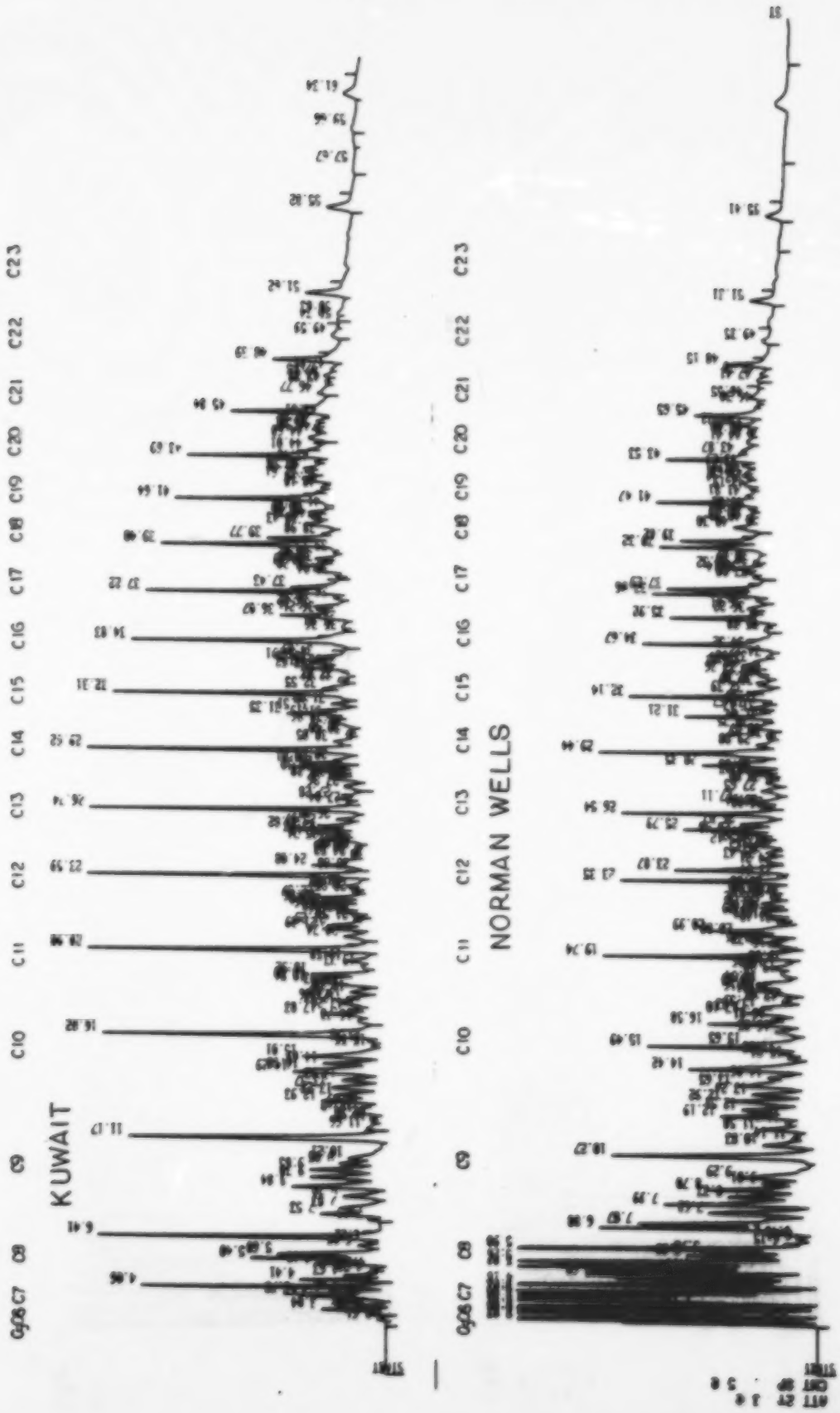
	THICK	SHEEN	TOTAL
ACTUAL OIL DISPERSED	8.571428	.4477647	9.019192
PERCENT DISPERSED	44.64286	55.9706	45.09597
REMAINING OIL VOLUMES (m3)	10.62857	.3522352	10.98081
REMAINING OIL THICKNESS (mm)	.5314286	4.40294E-03	.1098081
WATER CONCN TIME ZERO (ppm)	214.2857	2.79853	45.09597
WATER CONCN MEAS TIME (ppm)	185.7081	2.79853	39.38044
OIL REMAINING DISPERSED	7.428324	.4477647	7.876089
PERCENT REMAINING DISPERSED	38.68919	55.9706	39.38044

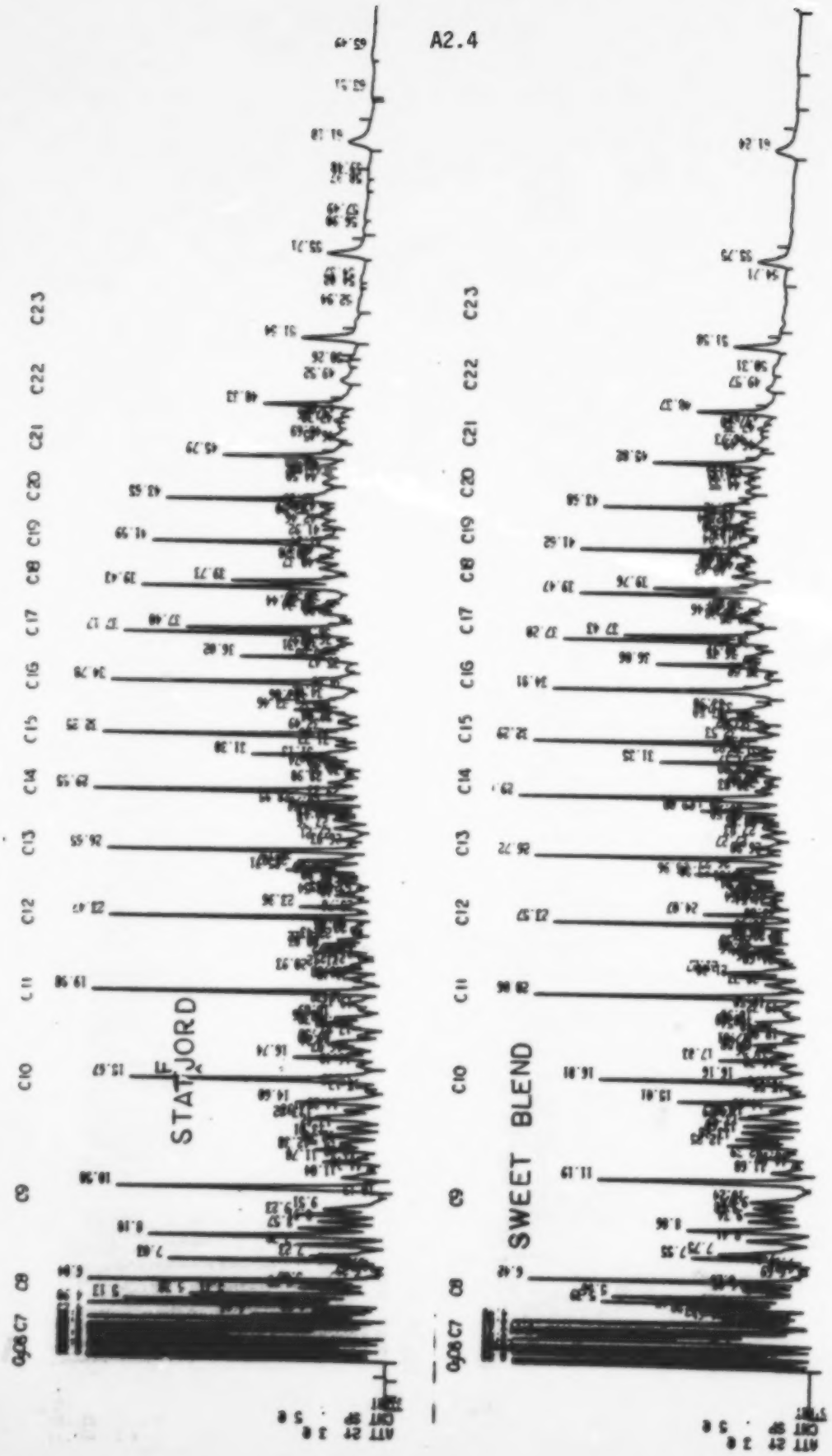

C6,C8 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C23
ARABIAN LIGHT
C6,C8 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C23
ARABIAN HEAVY

A2.1


C6 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C23
EKOFISK
C6 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C23
EPS

A2.2

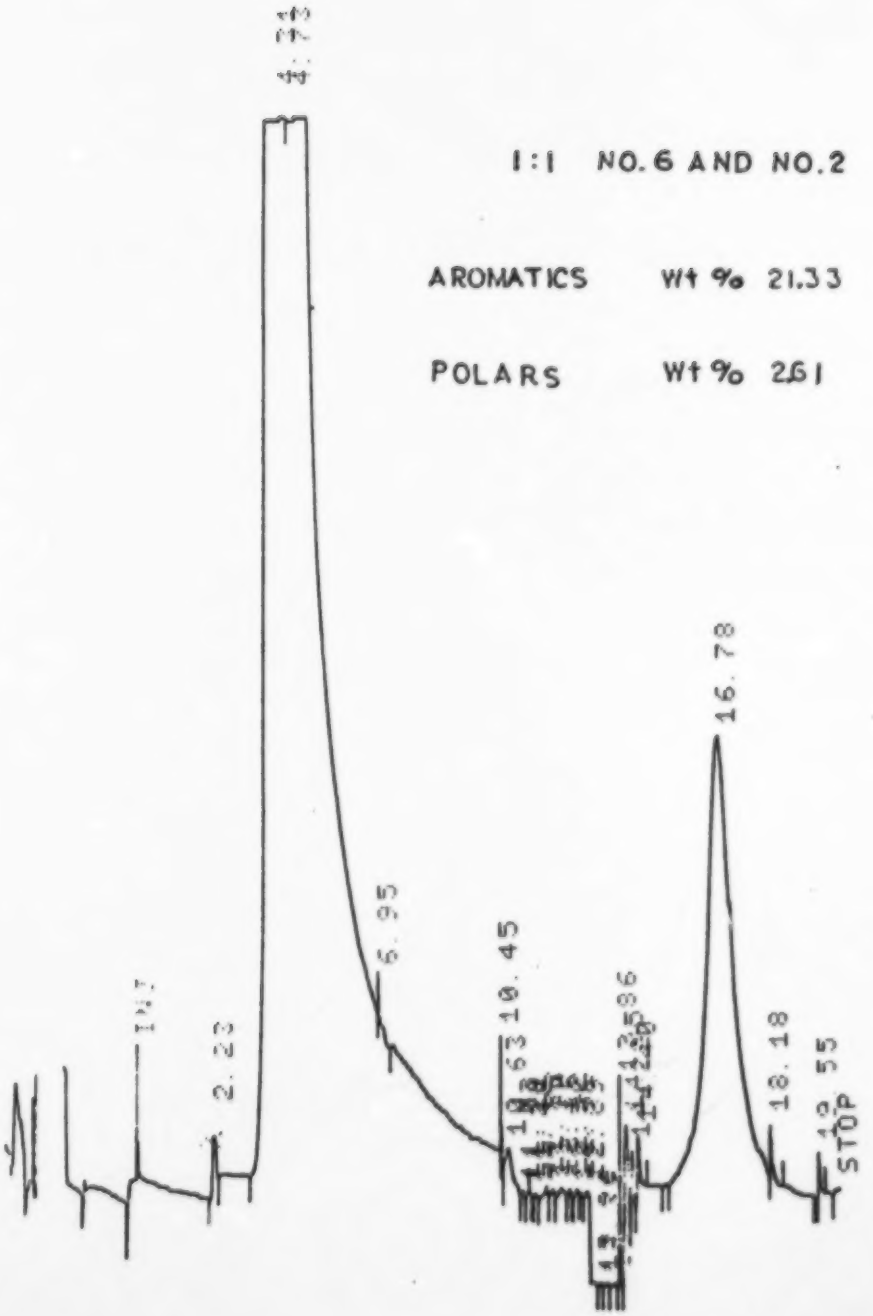

KUWAIT
NORMAN WELLS
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16
C17
C18
C19
C20
C21
C22
C23

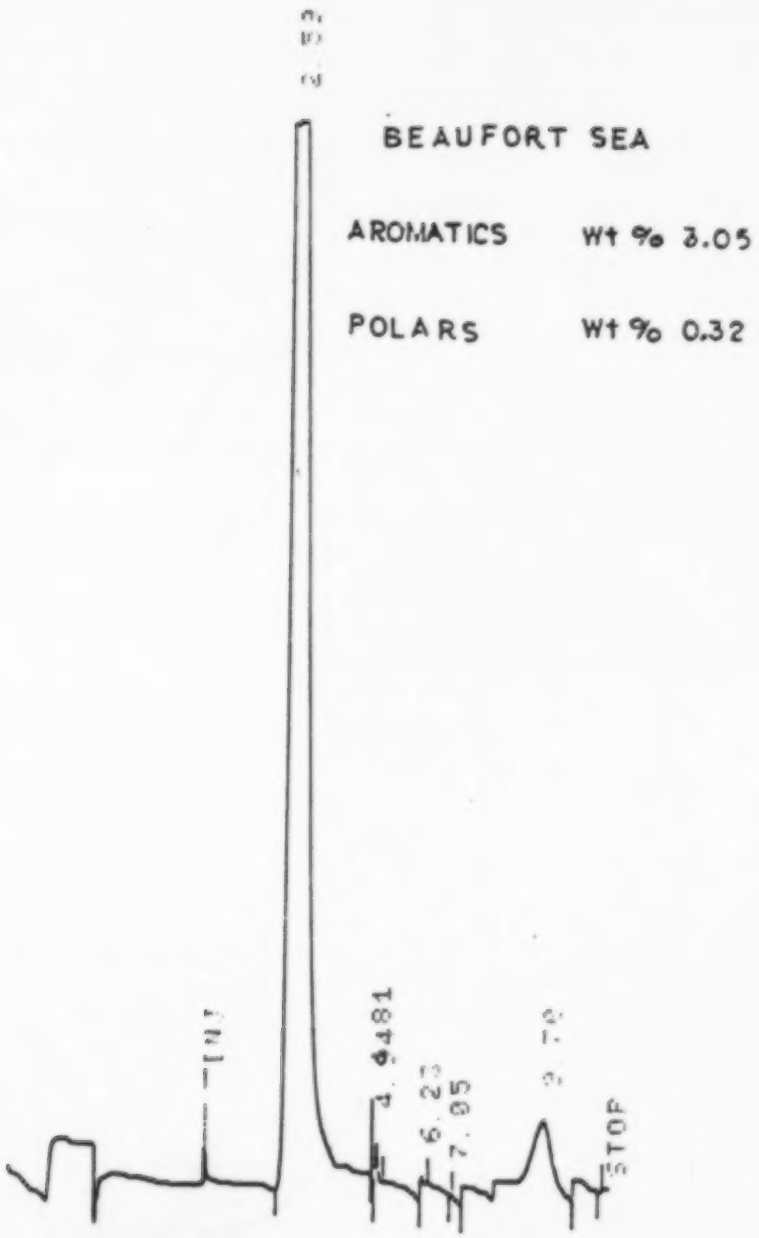

STATJORD
SWEET BLEND
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16
C17
C18
C19
C20
C21
C22
C23

1:1 NO.6 AND NO.2

AROMATICS Wt % 21.33

POLARS Wt % 2.61

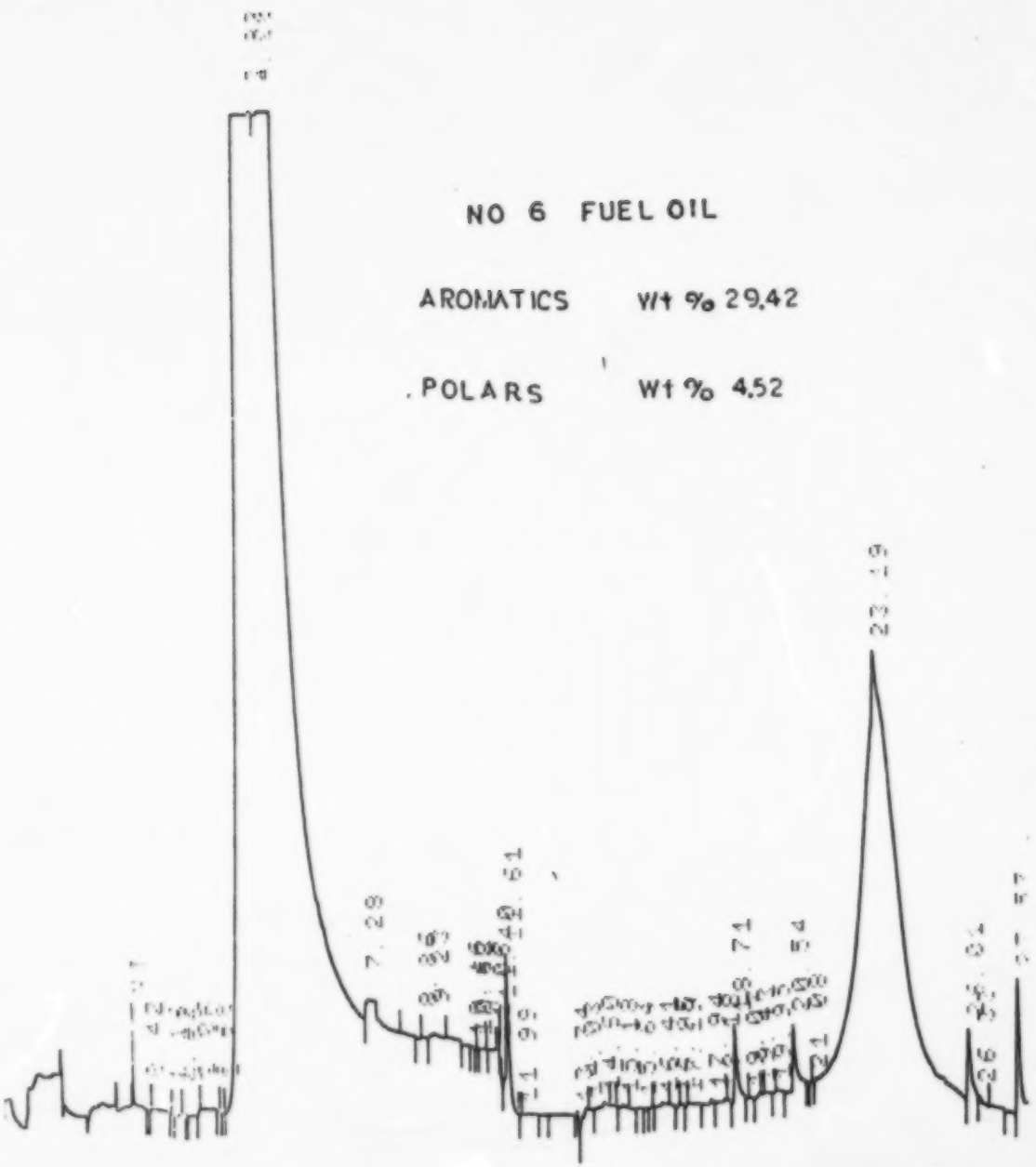



BEAUFORT SEA
AROMATICS Wt % 3.05
POLARS Wt % 0.32
INT
4.4481
6.23
7.85
STOP

NO 6 FUEL OIL

AROMATICS Wt % 29.42

POLARS Wt % 4.52

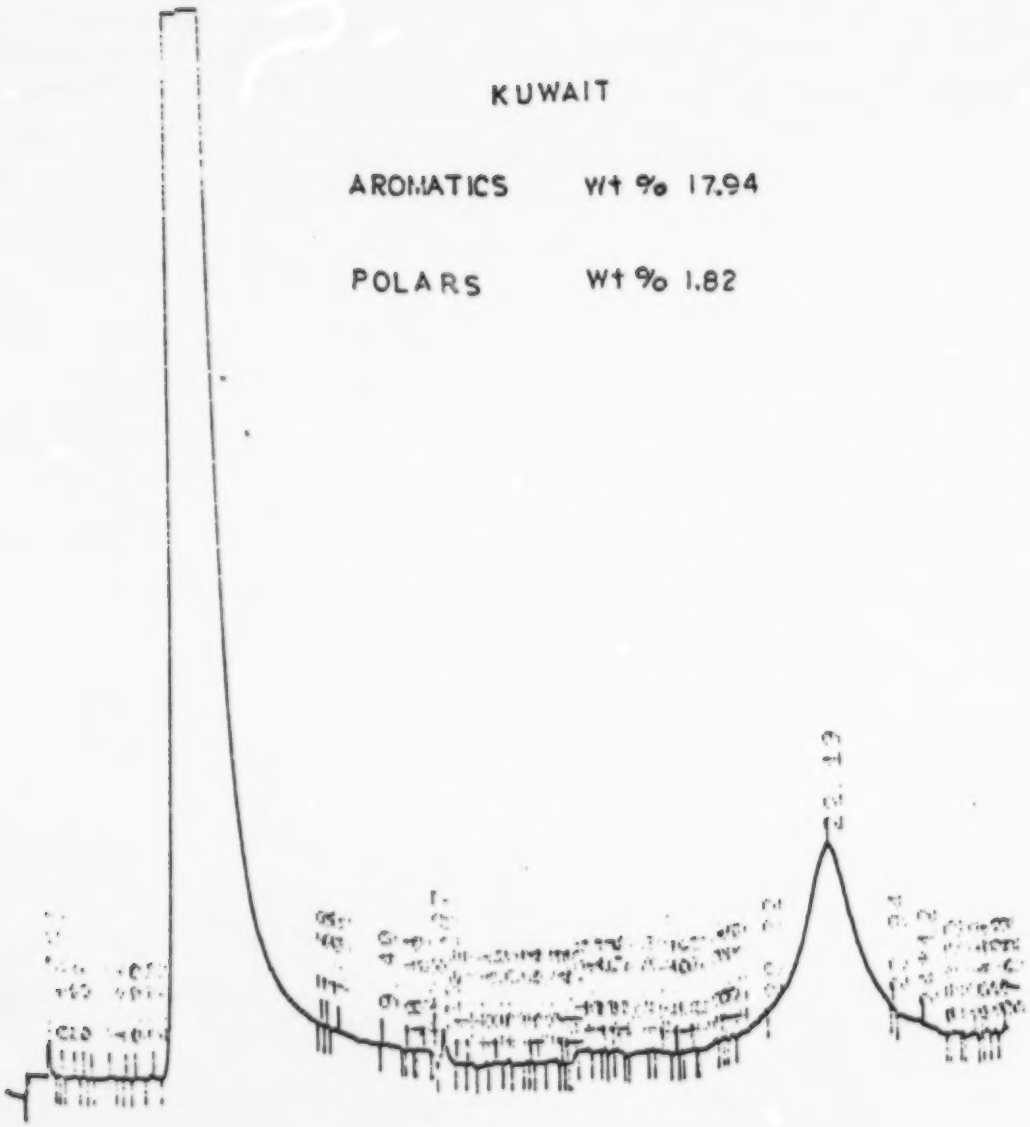


042

KUWAIT

AROMATICS Wt % 17.94

POLARS Wt % 1.82

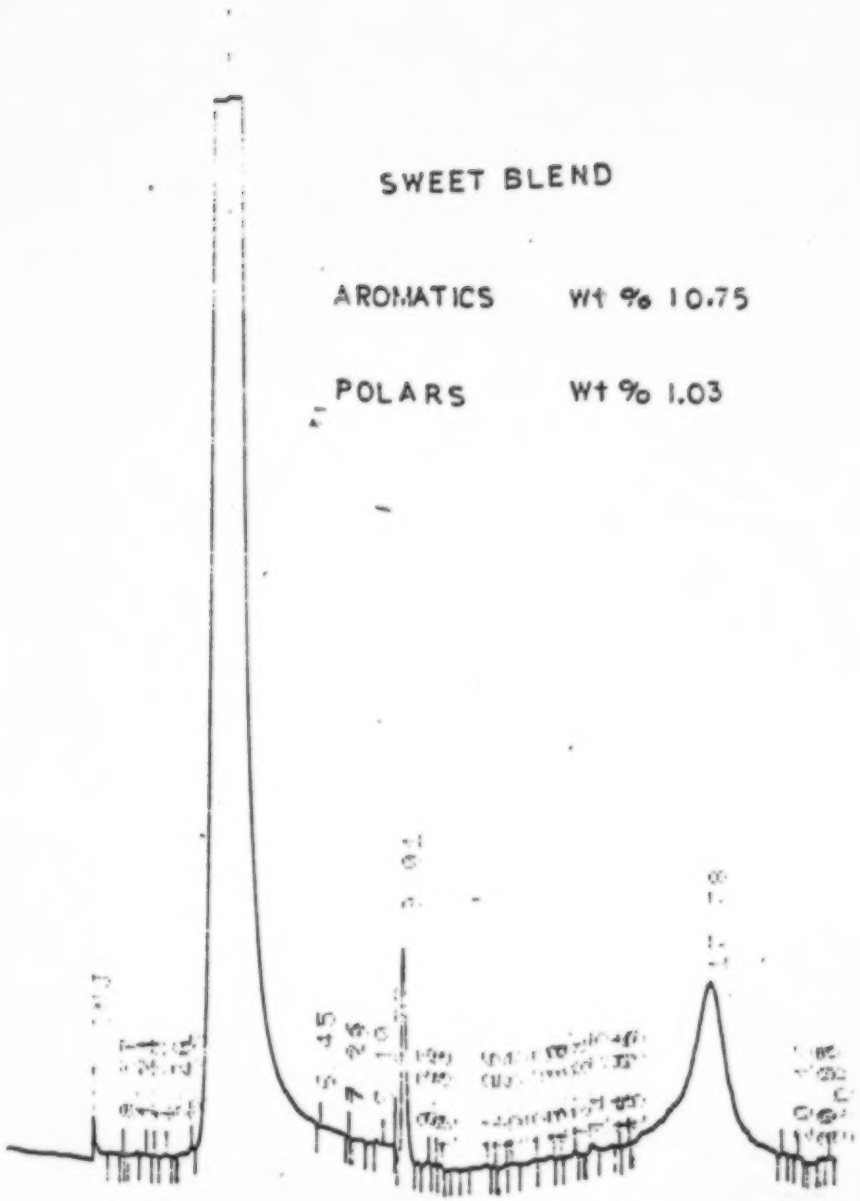


040

SWEET BLEND

AROMATICS Wt % 10.75

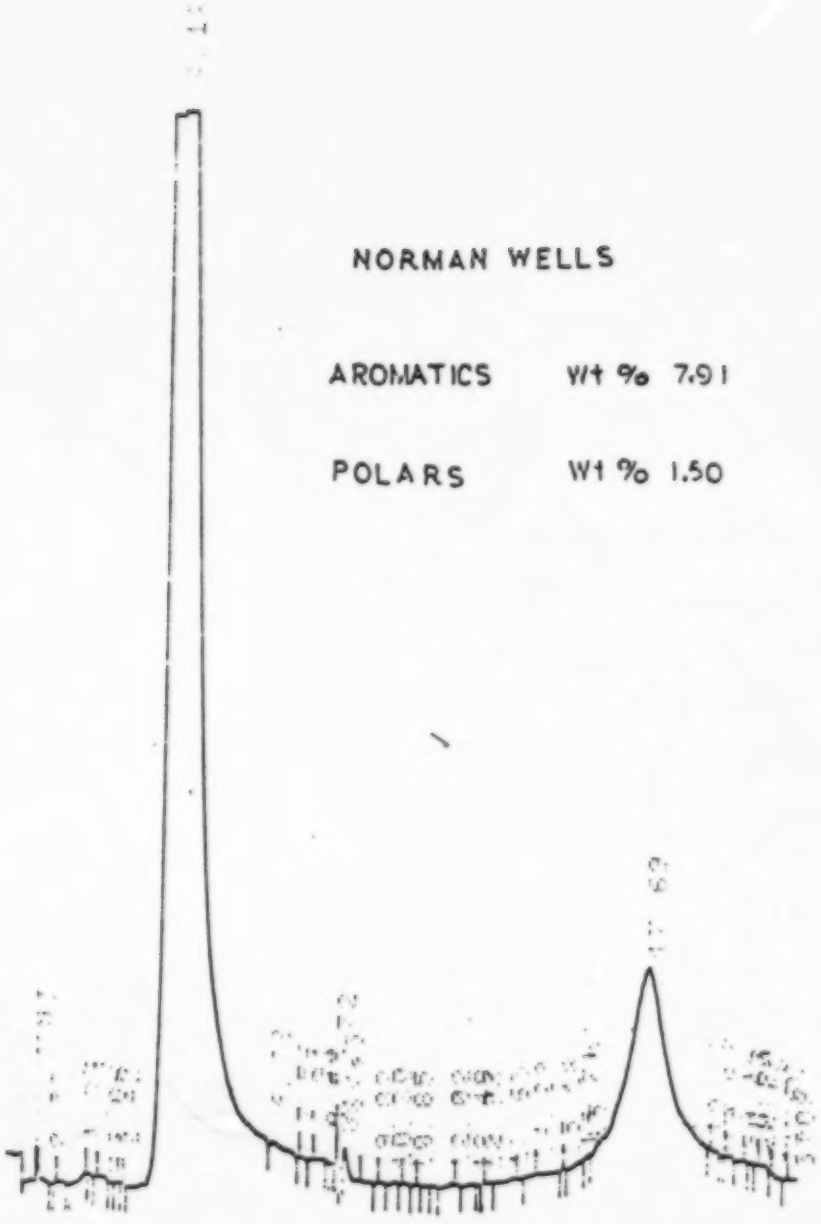
POLARS Wt % 1.03

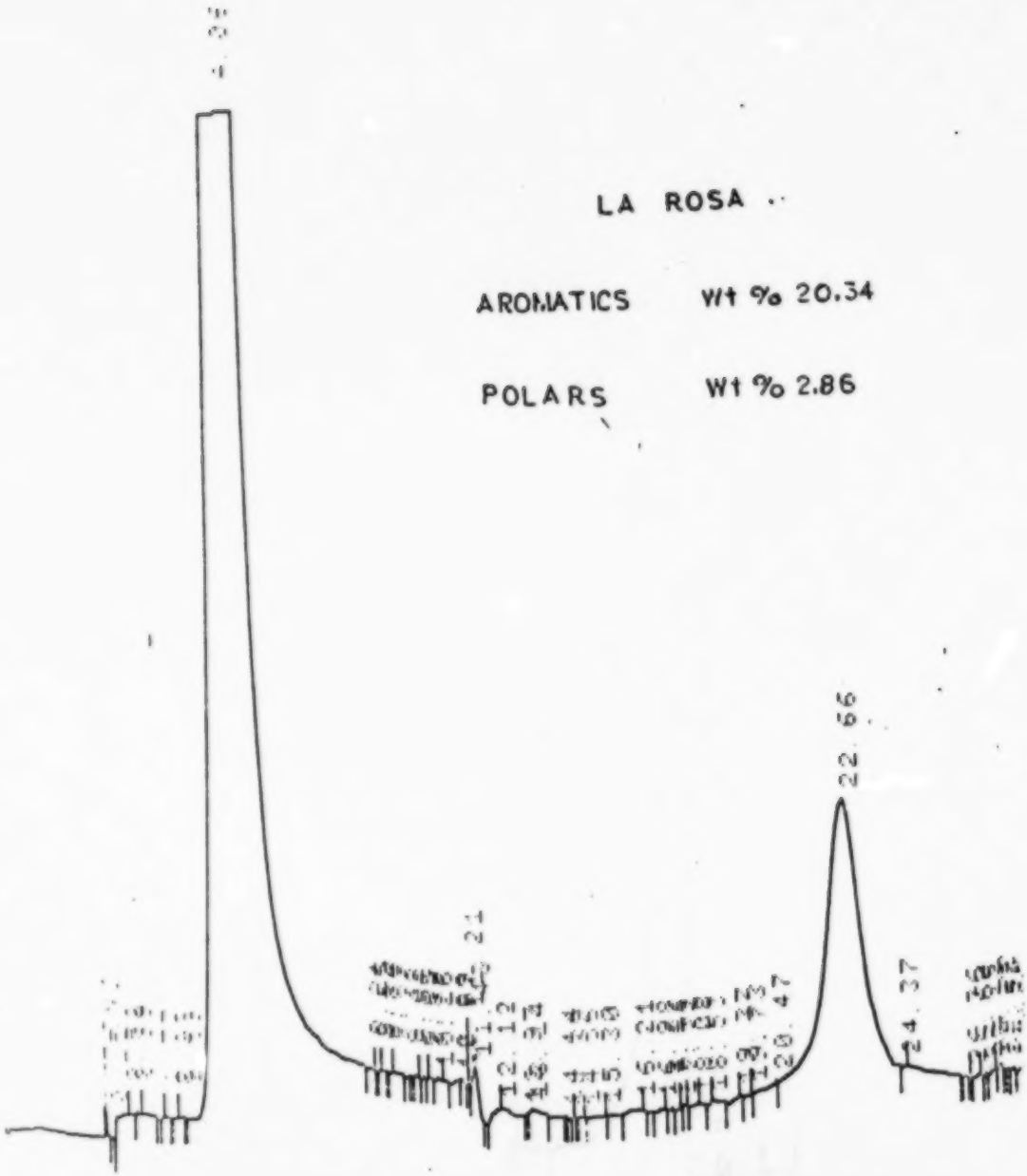


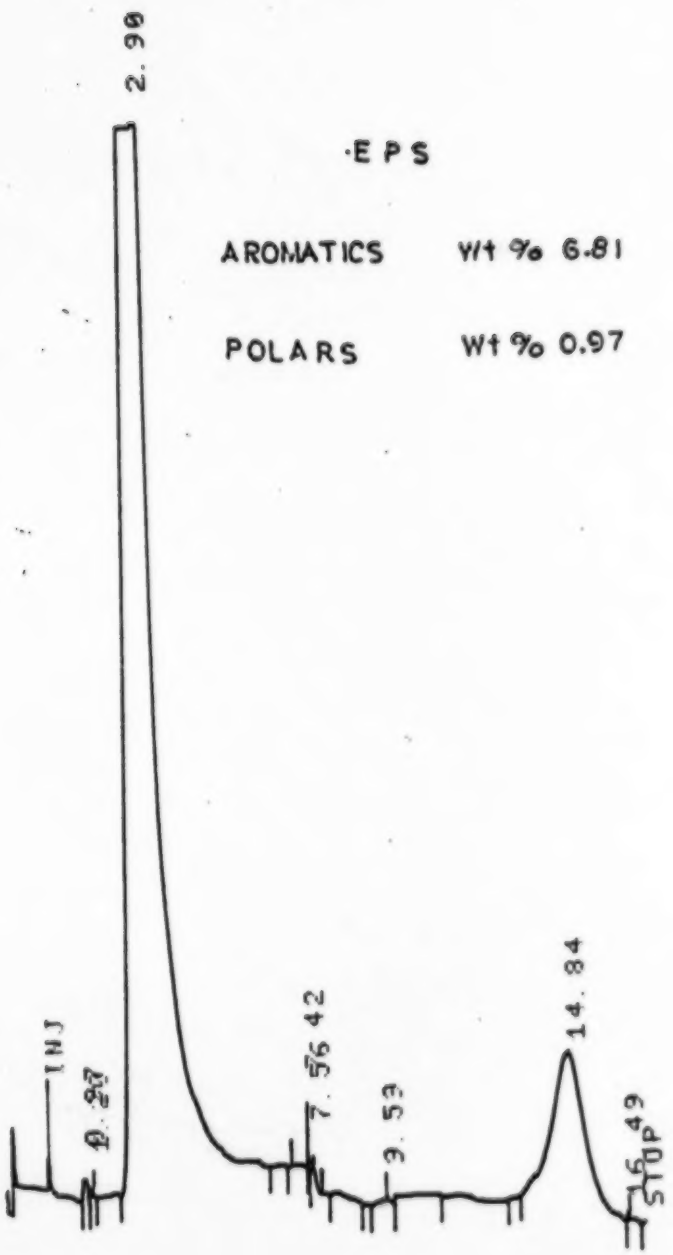
NORMAN WELLS

AROMATICS Wt % 7.91

POLARS Wt % 1.50



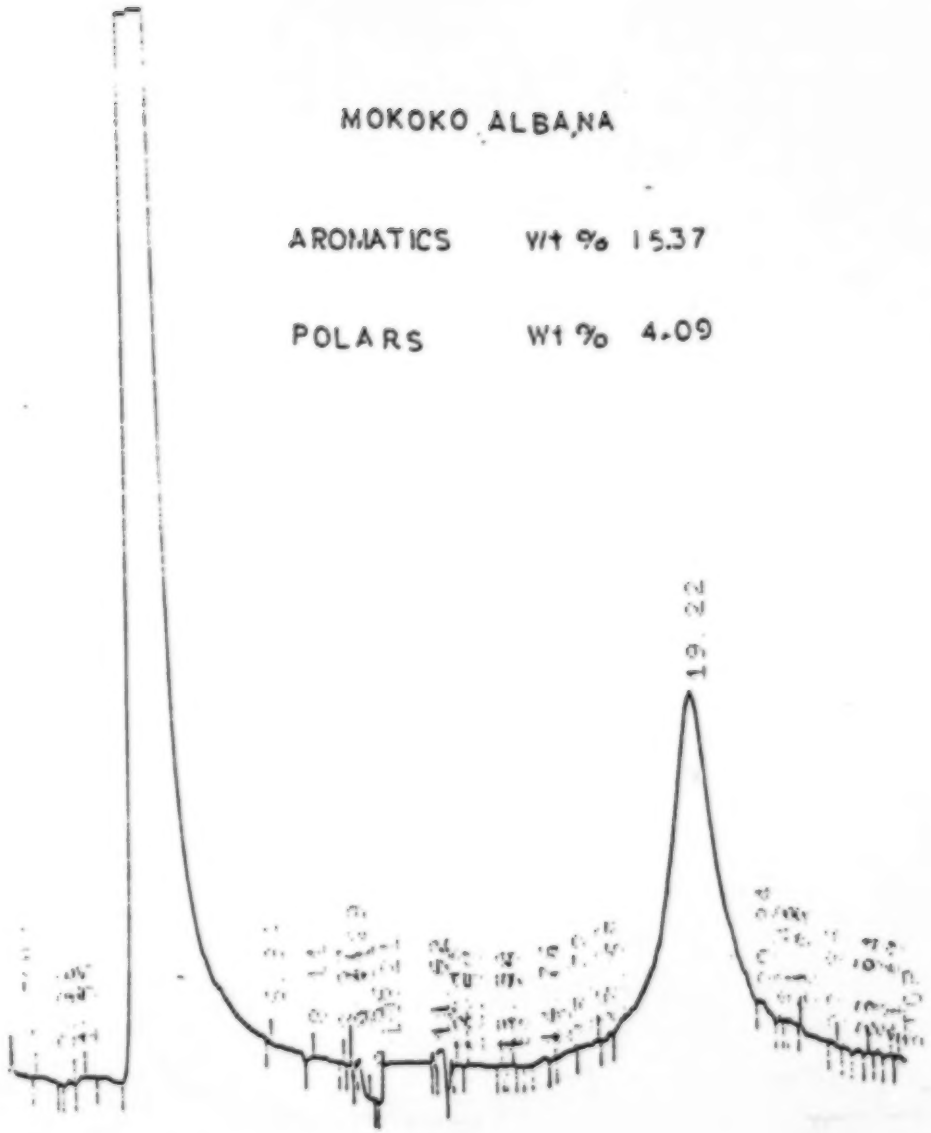

LA ROSA
AROMATICS Wt % 20.34
POLARS Wt % 2.86


2.99
EPS
AROMATICS Wt % 6.81
POLARS Wt % 0.97
INJ
0.27
7.56
42
3.53
14.84
STOP
49

MOKOKO ALBANA

AROMATICS Wt % 15.37

POLARS Wt % 4.09



ARABIAN HEAVY

AROMATICS Wt % 18.19

POLARS Wt % 1.75